Hierarchical Orientational Relaxation Inducing Shish-Kebab Formations in Polymer Melt Crystallization

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We studied athermal relaxation of bulk extended chains by means of dynamic Monte Carlo simulations, and we got intermediately relaxed melts with a memory of chain orientations but no more crystalline order. The orientational memory in the melts dominated the crystal orientation and nucleation types. The difference in crystallization behaviors induced by orientational relaxation suggested the mechanism of hierarchical crystallization. Thus, we studied the isothermal crystallization of a binary blend of different relaxed chains. We observed the prior crystallization of less relaxed chains could act as a shish to induce epitaxial crystallization of more relaxed chains to form kebabs. This mechanism had demonstrated the structure of precursors and gave insight into the formation of shish-kebab crystals in polymer melts. The results suggested that in flow-induced polymer crystallization the hierarchical orientational relaxation of chains decided the formation of shish-kebabs.

Introduction

Polymer melt crystallization is typically nucleation controlled. The initiation of crystallization via crystal nucleation has a threshold of crystalline size, where the body energy gain should overcome the surface free energy penalty in their contributions to free energy changes.[1] Naturally, there were two ways to enhance crystal nucleation. The first way is by decreasing the surface energy penalty, commonly realized by introducing a foreign substrate of high affinity and switching to heterogeneous nucleation, such as self-nucleation.[2] The second way is by increasing the body energy gain in order to decrease the conformational entropy, usually through making a mechanical manipulation to polymer chains and letting them extend. A typical case in this way is flow-induced crystallization.[3]

Polymer melt crystallization under a shear/elongation flow is quite general in the processing of semicrystalline polymers.[4–7] An effect of flow on polymer melt is often the occurrence of hierarchical crystal morphology (shish-kebab); as observed in experiments, some stretched chains form the extended-chain crystals acting as a shish and then kebabs consisting of the folded-chain crystals grow on its lateral surface.[8] This precursor may eventually develop into a stack of thin lamellae growing radially outward from a central fiber.[9,10] The shish-kebab crystallites have been found to be a general initial crystal structure at the early stage of polymer melt spinning.[11]

Recently, shear-induced shish-kebab precursor formation in polymer melts has received much attention. The precursor structure was suggested to be a scaffold (network) of stretched chains (or chain segments) that could be in the amorphous, mesomorphic, or crystalline state.[10,12,13] These high oriented structures mainly formed by high-molecular-weight species, which was regarded to play an important role in orienting the melt and in observing the precursor formation. So the molecular weight and molecular weight distribution were revealed to produce the pronounced effect in shear-induced crystallization.[14–17] In addition the experiments on shear-induced crystallization of branched isotactic polypropylenes (iPPs) investigated the effect

of the molecular architecture on the nature of orientation-induced precursor structures and conjectured the highly branched species took part in the formation of precursors of primary nuclei for crystallization.[18] Up to now, the intrinsic mechanisms of precursor formation behind these characters (polydispersity in chain length and molecular architecture) has not been well understood.

Polymer chains keeping in a random coil conformation is the most stable state whether for an isolated polymer or bulk polymers.[19,20] Naturally, the stretching of chains is potentially followed with a reverse relaxation. The shear/elongation flow would induce conformation ordering and relaxation in polymer melts.[21,22] So there came a question: which process of polymer chains decided the precursor formation, the stretching or the relaxation? Experiments on binary polymer blends of different chain length reported that the life period of long-chain precursors decreased with increasing temperature and the length of the shish decreased with time.[23,24] Furthermore, shear-induced structures formed by long-chain components were reported to be related to the matrix viscosity.[24] Especially the branched component introduced to the polymer melt would take part in the precursor formation and promote the stability of precursor structures.[18] On the other hand, there would be no crystallization occurring during the drawing of poly(ethylene terephthalate) (PET) when the stretching rate is higher than the chain retraction motion.[25] These experimental results reflected the features of chain relaxation and, therefore, suggested the relaxation played a key role in the precursor formation for polymer melt crystallization.

Molecular simulations have been widely used to investigate the microscopic origin of precursors. Molecular dynamics simulations have demonstrated by uniaxially drawing an isotropic glassy state an oriented polyethylene melt formed[26] and then a fast crystallization was induced.[27] Langevin dynamics simulations have well reproduced the flow-induced shish formation and the subsequent kebab growth on the shish.[28] We used dynamic Monte Carlo (MC) simulations that even demonstrated that the shish could be so small as a single prealigned chain in polymer solution, while in polymer melt crystallization neither orientational relaxation nor polydispersity in chain length

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was indispensable for the precursor formation. In this Article, by means of dynamic Monte Carlo simulations, it will be shown that the highly oriented amorphous chains with no more crystalline order could act as a shish to induce the irregular coils to form kebab crystallization on the shish's surfaces. The hierarchical orientation relaxation would introduce a difference in crystal orientation as well as the nucleation type and then produce hierarchical crystallization in the polymer melt. Our simulation results, therefore, reveal that it is the hierarchical orientation relaxation that decides the formation of shish-kebab in flow-induced crystallization.

In this Article, after a simple introduction of simulation techniques, we first study the athermal relaxation of bulk extended chains and prepare different relaxed melts in which no more crystalline order remains but differential orientational memory exists in every melt. Then we investigate the crystal orientation and nucleation type in isothermal crystallization from different relaxed melts. After that, we study the precursor formation in a binary blend of different relaxed chains. Finally, we provide conclusions.

Simulation Techniques

Dynamic Monte Carlo simulations of lattice polymer chains has been widely used to study the phase behaviors in polymer system, such as chain relaxation,[29,30] microphase separation,[31,32] microstructure transition,[33,34] nucleation and crystallization.[35–38] In our Monte Carlo simulation method, a series of consecutive occupations represented a polymer chain, while the single voids could be regarded as free volume in a bulk phase or solvents in polymer solution. We relaxed the chain conformation through a microrelaxation model in a cubic lattice box with periodic boundary conditions. The model could be described as a single-site bond fluctuation model with the addition of a slithering diffusion terminated by extending the nearest kink conformation along the chain.[31] The bonds were allowed to align either on the lattice axes or on the face and body diagonals, so the bond orientations could be as much as 13. The interactions between local chain units could be simplified into hard-core volume exclusion and various short-range attractions. The attractions resulted from a collinear connection of consecutive bonds along the chain (E_c) and a parallel alignment of two crystallizable bonds (E_p). The former reflected the rigidity of a polymer chain, and the latter drove the polymer to crystallize. In each step of microrelaxation, Metropolis sampling was employed with a potential energy penalty $(cE_c + pE_p) = (c + pE_p/E_c)E_c$, where c is the net number of noncollinear connections along the chain and p is the change in the number of nonparallel packing of two bonds. So the crystallinity could be defined as the fraction of bonds containing more than five parallel neighbors (the critical value of five represented the status of a bond changing from an amorphous to a crystalline phase). Simply, we fixed $E_p/E_c = 1$ and only adjusted kT/E_c with the system temperature, where k is the Boltzmann constant and T is the temperature.

Results and Discussion

A. Athermal Relaxation of Bulk Extended Chains. In a 64^3 cubic lattice box, we layer-by-layer regularly put 2048 chains along the x axis. Each chain contained 120 units with once-folded extended conformation. The snapshot of the bulk extended chain sample can be seen in ref 39. The extended conformation of bulk chains could be regarded as a consequence of crystallization or impulse stretching under shear/elongation flow fields. After an athermal relaxation without any potential energy, we traced the time evolution of the components of the
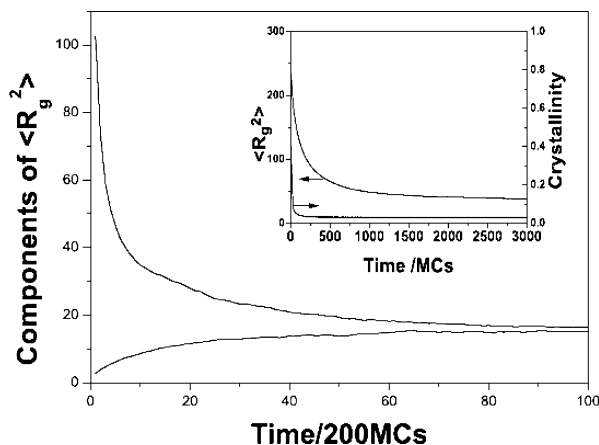
Figure 1. Time evolution curves of the components of the mean-square radius of gyration during the athermal relaxation of bulk extended chains. The upper curve corresponds to the z component parallel with the extended orientation, and the other is the vertical component (x or y). The inner picture shows the time evolution of the total mean-square radius of gyration and crystallinity.

mean-square radius of gyration parallel (along the z axis) and vertical to the initial extended direction (parallel with the x or y axes).[37]

The results of chain orientation relaxation are shown in Figure 1. The relaxation step was taken every 200 MC cycles (each MC was defined as one trial move for each monomer averaging over the sample system). From the inner inset of Figure 1, we find that the coil size markedly relaxed much slower than the crystallinity. So during the process of relaxation there existed intermediately relaxed melts, at which the elimination of the crystalline order had been saturated but the coil shapes were still anisotropic to maintain the orientational memory of the initial state.

The athermal relaxation process in our simulations had some qualitative meaning to the real polymer chains. It is well-known that polymer ordering comprises intermolecular positional and orientational order as well as intramolecular conformational order.[40] So the relaxation of an extended chain contains two steps: segmental relaxation and molecular relaxation. The change in intermolecular positional and orientational order corresponded to the segmental relaxation of chains, which could be described by the parameter of crystallinity, while the molecular relaxation reflected the evolution of intramolecular conformational order, which could be represented by the gyration of chains. In the intermediately relaxed melts, polymer chains practically remained in the stage of molecular relaxation with the segmental relaxation accomplished.

In fact, the intermediately relaxed states existed in real polymer systems. It had been reported that, during the fast quenching of stretched PET, an amorphous state with a definite global chain orientation but nearly random bond orientations could be frozen by the glass transition.[41] Molecular dynamics simulations even demonstrated there existed such a kind of intermediate state during the orientational relaxation of a single extended polyethylene.[42]

B. Isothermal Crystallization. Orientational memory in a macromolecular melt could lead to enhanced nucleation and crystallization. Because a more extended chain would have lower entropy but changes only little in enthalpy, the melting temperature accordingly increases. At a given crystallization temperature, an oriented macromolecule might have thus a larger supercooling and greater driving force toward nucleation and crystallization. In our former simulations, we verified that the
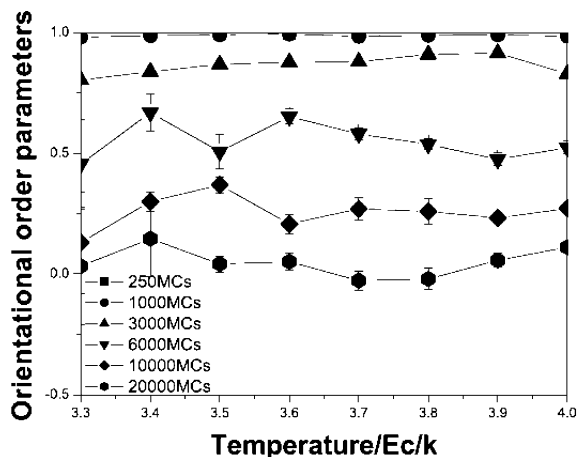
Figure 2. Orientational order parameters obtained from saturated isothermal crystallization at variable temperatures in different intermediately relaxed melts. The data were averaged over five individual experiments (with different seeds of random number generation). The segments were drawn to guide the eyes.

orientational memory indeed introduced a much faster crystallization in the bulk polymer phase. The experiments on shear-induced crystallization of iPP melt really exhibited the half-time of crystallization, decreasing with an increasing conformational ordering of chains.[43]

The key product during flow-induced crystallization was the oriented crystallization along with the flow direction. Experiments on shear-induced molecular extension and crystal orientation in iPP melt demonstrated that the relaxation time for the sample was estimated to significantly affect the subsequent crystal orientation.[44] And the crystallization of polypropylene after orientational relaxation revealed that the size of the domain consisting of lamellae parallel with the shear direction increased in spite of the cessation of radial growth.[45] Here we would devote some effort to find the correlation between crystal orientations and the orientational relaxation of chains. We exposed the different intermediately relaxed melts to variable temperatures. The crystallization process was monitored by the overall crystallinity. After isothermal crystallization had been saturated (that is, the crystallinity was more than 0.5 and no more significant increase), we evaluated the crystal orientations.

Figure 2 shows the orientational order parameters obtained from saturated isothermal crystallization at variable temperatures in different relaxed melts. The orientational order parameters of crystalline bonds were defined as $P = (3 < \cos^2 \theta > -1)/2$ by summing those crystalline bonds containing more than five parallel neighbors,[46] where the angle θ was read with reference to the initial extended direction and $\langle \cdots \rangle$ meant an assembly average over all the crystalline bonds containing more than five parallel neighbors. According to this definition, if all the concerned bonds were parallel with the initial orientation, then P was equal to 1; if they were perpendicular, then P would be -0.5; and if they were random, then P was close to zero. From Figure 2, one could see that the crystallization from the melts relaxed 250MCs and 1000MCs gave rise to a strong tendency of parallel orientations. The orientational order parameters decreased with the prolonging relaxation of the melts, and the crystals from the 20000MCs-relaxed melt showed random orientations. Moreover, all the crystal orientations were observed to change little with temperature. The results demonstrated that the extent of orientational relaxation dominated the degree of orientation in crystallites.

Higher orientation in melts led to higher crystal orientations. More details on the nucleation and growth of the oriented

structures would be obtained by analyzing the overall crystallization. As a phenomenological description of isothermal crystallization, the Avrami equation $1 - X_c = \exp(-Kt^n)$ treated the time (t) evolution of the relative crystallinity (X_c). The Avrami index n revealed the characteristic of the nucleation type as well as the crystal growth geometry. And the kinetic constant $\ln K$ reflected the overall crystallization rate. In an athermal type of nucleation in three-dimensional growth, for $n \leqslant 1$, a fibrillar crystal growth was expected; for $n \leqslant 2$, it was expected to be circular lamellae; and for $n \sim 3$, it was spherelike.[1] In polymer crystallization from melt, noninteger values of n were often obtained, indicative of an overlap of different crystal growth geometries.[18]

Figure 3 gives the analysis by Avrami models varying with crystallization temperatures. For the isothermal crystallization from high orientated melts (250MCs and 1000MCs), the Avrami indices stayed at no more than one. Such a small fractional index implied a massive nucleation induced by alignment of the chains, which was indicative of fibrillar crystal growth in the polymer melt. The Avrami index 0.5 had been reported for the synchronous crystallization confined in disconnected micro-domains of block copolymers.[47,48] Moreover, for these oriented melts, the chain conformation approached the final macroconformation in the crystalline state, so a greater driving force toward nucleation and an enhanced rate of crystallization was expected; as shown in Figure 3b, the crystallization rates were higher than those from other more relaxed melts. However, for the other more relaxed melts, the homogeneous nucleation under low temperature demonstrated an apparent first-order kinetics ($n = 1$), as observed in the isothermal crystallization confined in one dimension.[49,50] And the Avrami indices distinctly increased with the crystallization temperature, which could be attributed to the greater extent of crystal growth allowed by the decrease of nucleation density at higher temperature.[51] Anyway, the orientation in melt was estimated to dominate the geometry of crystal growth.

The shear-induced crystallization in the polymer melt demonstrated that the long chain branched introduced in iPP melts gave rise to a decrease in the Avrami index from 3 to 1.8, indicative of unoriented spherulitic crystal growth switching to a rod/disklike crystal growth.[18] And in the crystallization of iPP under fast short-term shear, the value of the Avrami exponent was further decreased to 1.36, which could be attributed to the growth of both fibrillar and disklike crystal.[52] On the other hand, increasing high-molecular-weight component in the polyethylene blend could keep one-dimensional growth of oriented structure.[53] These results demonstrated that the crystal growth geometries could be changed by introduction of a high-molecular-weight component or branched component.

C. In a Binary Blend of Different Relaxed Chains. A high-molecular-weight component or branched component can keep the orientational memory longer than other components, and the memory offers the priority in crystallization, which acts as precursors and induces the shish-kebab crystallization in polymer melts. In our former simulations about the polymer blend with different chain lengths, after orientational relaxation for the same period, we really that found the precursor formation selected the long-chain component.[39] However, why was polydispersity in chain length or architecture needed to form a shish-kebab structure? And what is the intrinsic mechanism for precursor formation? The role of polydispersity in chain characters in flow-induced oriented crystallization was to produce hierarchical orientational relaxation, enhanced by the overlap or entanglement of these

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(a)

(b)
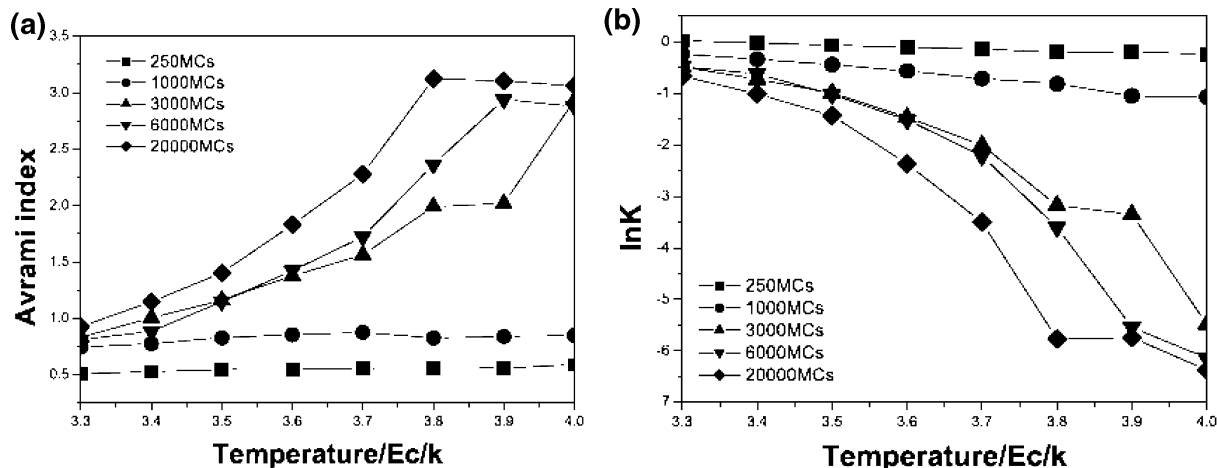
Figure 3. Avrami index (a) and kinetic constant (b) obtained by Avrami analysis of isothermal crystallization from different intermediately relaxed melts at variable temperatures. The data were averaged over five experiments as in Figure 2. The segments were drawn to guide the eyes.
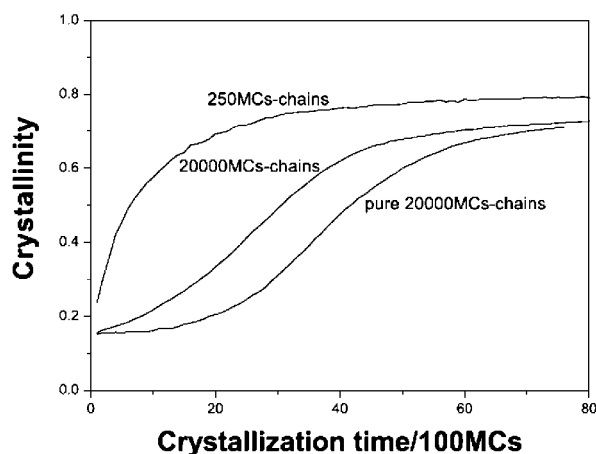
Figure 4. Time evolution curves of crystallinity for two components in the binary mixture and for the pure more relaxed melt, as labeled in the figure, at the temperature $T = 3.8/E_c/k$.

chains. So we could deduce that it was the hierarchical orientational relaxation that induced hierarchical crystallization. Based on this deduction, we would go beyond the concrete experiments and study the key process. We directly constructed a binary blend of different relaxed chains to observe the subsequent crystallization. The initial mixture was designed by relaxing the first four layers for 250MCs and the remaining 60 layers for 20000MCs. According to Figure 1, we could see there was no crystalline order remaining in the mixture while the relaxation of 20000MCs-relaxed-chain component had already been saturated but the 250MCs-relaxed-chain component was not.

The isothermal crystallization of 20000MCs-relaxed chains in the binary mixture appeared much faster than that in the pure 20000MCs-relaxed chains, and this acceleration could be attributed to the prior crystallization of the 250MCs-relaxed-chain component, as shown in Figure 4. Figure 5 provides snapshots at 1700MCs of crystallization, demonstrating that the present less-relaxed-chain crystals facilitated the crystallization of the more relaxed chains. The less-relaxed-chain component had the priority in crystallization and formed a superstructure consisting of oriented crystals acting as shish, onto which the more relaxed chains just started their crystallization from the lateral sides by means

of epitaxial crystallization. The parallel outgrowth of the multilayer crystals produced kebabs. Recently, experiments on shear-induced precursor and crystallization reported that the precursors really existed with fibrillar morphology and no crystallinity. When flow stopped, they first crystallized and then assisted the crystallization of the rest of the polymer, leading to the formation of shish-kebabs.[52]

The above observation on the binary blend of different relaxed chains suggested that the source of precursors was the oriented noncrystalline component, which would be prior to crystallization and induce the formation of shish-kebabs. The hierarchical crystallization resulted from hierarchical orientational relaxation, which could be realized by polydispersity in chain length[54] or in molecular architectures[18] or differences in chain flexibilities,[55] or some other way. However, it was expected that hierarchical orientational relaxation was the key process to form shish-kebabs structures in flow-induced crystallization.

The hierarchical orientational relaxation of polymer chains could induce hierarchical crystallization in polymer melt crystallization, but the details of the shish-kebab formation had not been well understood. So we designed two experiments as follows: (1) We used more relaxed chains such as 1000MCs-relaxed chains to replace 250MCs-relaxed chains as the high oriented component and then observed the isothermal crystallization at the same temperature, but there was no precursor found. This result demonstrated that the orientations of the polymer chains must be high enough to construct the precursor structure. (2) We exposed the binary blend of hierarchical orientation to another crystallization temperature lower than $3.8/E_c/k$, and there was no precursor either. Such a result would give us greater insight into the nucleation mechanism in the formation of shish-kebabs. As for our simulated binary blend of hierarchical orientation, the highly oriented chains first formed the fiberlike crystals (shish). Then the irregular coils just began their crystallization from the lateral side of the shish by means of epitaxial crystallization to produce the kebab. The growth of the kebab induced by the shish in the melt could be regarded as a case of self-nucleation. This process revealed the necessary sequence of crystallization of the shish and kebab; that is to say the nucleation types and crystallization rates must be different to form hierarchical crystallization. So the crystallization temperature must be high enough to allow the highly oriented chains to first undergo fibrillar nucleation and then
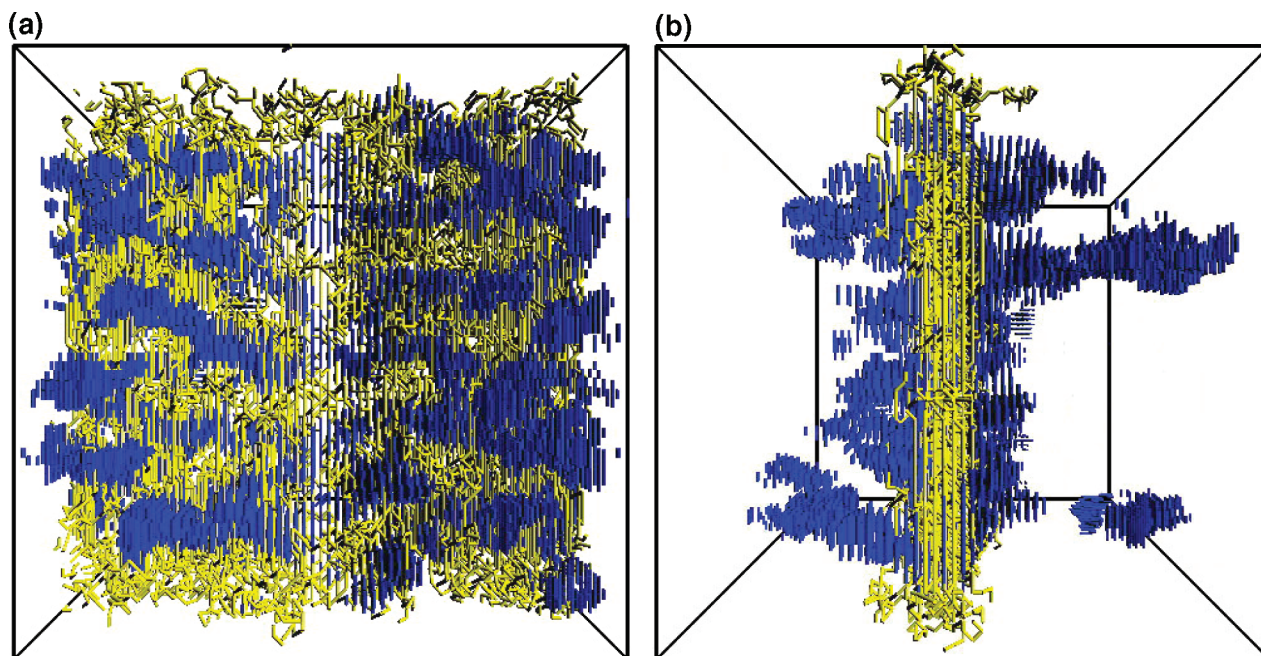
Figure 5. Snapshots of the crystallites at the instance of 1700MC cycles during the isothermal crystallization of the mixture at the temperature $T = 3.8/E_c/k$. For the less relaxed component, all the chains are in yellow, while for 20000MCs-relaxed chains only the bonds containing more than 18 parallel neighbors are in blue. All the bonds are shown in cylinders. (a) View from x axis; (b) view from y axis, the separate crystallite existed due to the periodical boundary conditions.

induce the rest of the polymers to begin secondary nucleation and form the folded-chain crystals. Based on the discussion above, we found that the two requirements could be satisfied by hierarchically oriented melts and therefore suggest that the hierarchical orientational relaxation induced shish-kebab formation in polymer melt crystallization.

Conclusions

It was natural to observe the orientational relaxation after the flow stop. Experimental observation suggested that the occurrence of precursors should be related to the relaxation process. Molecular simulations provided the possibility to study the role of orientational relaxation in precursor formation and the details of shish-kebab structures.

We summarize this paper as follows. First, through athermal relaxation of bulk extended chains, we got different relaxed melts with differential orientational memory in coil shapes. Then we found the crystal orientation and nucleation type could be decided by the orientational memory retained in the different oriented melts. Based on the analysis of concrete experiments on shear-induced crystallization, we found that the sequences in crystal growth induced by hierarchical orientational relaxation could satisfy the precondition of shish-kebab crystallization. Then we constructed the hierarchically relaxed chains with a uniform chain length and studied the isothermal crystallization. We observed that the highly oriented component was prior to crystallization, which induced the epitaxial crystal growth of other random coils. This mechanism had demonstrated the structure of precursors and gave a good interpretation of the formation of shish-kebab crystals in the polymer melt. Our simulations verified the important role of orientational relaxation in flow-induced crystallization and suggested the decisive effect of hierarchical orientational relaxation in flow-induced precursor formation. Further discussions on the requirements of shish-kebab formation were provided to help in understanding the

mechanism and producing the hierarchical structures in experiments.

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