



Formation mechanism of reverse kebab structure inside hollow nanotubes studied by molecular simulations

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ABSTRACT

Formation of polymer crystals inside a hollow nanotube provides the potential for its interior functionalization. Based on dynamic Monte Carlo simulations, the formation mechanism of crystal lamellae with uniform orientation inside hollow nanotubes in polymer solutions was investigated. In nanotubes with lateral size smaller than the size of chain coils, inside segments prefer to orient along the long axis of the nanotubes, due to the confinement effect exerted by side surfaces. Thus, crystal lamellae with uniform orientation along the long axis of the nanotubes can be formed inside. Further investigations revealed that the formation of these reverse kebabs is codetermined by the degree of confinement and the strength of interfacial interaction. Both the increase of interfacial interaction and the decrease of lateral size can lead to the improvement of segmental orientation of inside segments, thus favoring the formation of the reverse kebabs.

1. Introduction

Recently, with the rapid developments of nanotechnology, the design and manufacture of polymer products in micro/nano scale have received widespread attention in both industry and academia [1–4], which have potential applications in microelectronics [5,6], device technology and drug delivery. However, physical properties of confined polymers are rather different from those of bulk polymers due to the changes of segmental dynamics [7–10] or microstructures [11–18]. Thus, understanding the mechanism of the effect of nano-confinement on polymer crystallization should be a prerequisite condition to achieve the regulation and control of physical properties of polymer materials in the nanoscale.

Generally speaking, there are three kinds of confined conditions corresponding to the restrictions imposed by geometries of different dimensionalities [19]. That is, polymers are confined in different geometries, i.e., films, tubes and spheres, corresponding to the one-dimensional, two-dimensional and three-dimensional confinements, respectively. Up to now, numerous researches have been carried out to investigate polymer crystallization behaviors in different confined states [19–26].

For the two-dimensional confinement, most work is focused on polymer melts confined within nanochannels or nanotubes

[22,23,26,27]. It was found that polymers exhibit anomalous crystallization behaviors as restricted into nanodomains [2,3,26]. The characteristic crystallization time of syndiotactic polypropylene confined in nanoporous alumina is much longer than that of the bulk polymer [26]. The change from heterogeneous nucleation to homogeneous/surface nucleation mechanism was detected by Müller et al. and Wang et al. in other crystalline polymers confined within nanoporous anodic alumina oxide [2,23,24].

However, polymer crystallization inside nanotubes in polymer solutions does not receive enough attention. The interior functionalization of nanotube can cause the changes of nanofluidic flow, and thus could be used for nanoscale chemical reactions, filtering and chromatography [28]. In general, delivering metal nanoparticles into the nanotubes is one of the most common methods for interior functionalization [29]. Recently, Fisher et al. found that nylon-11 can crystallize inside hollow carbon nanofibers in solutions after the treatment of ultrasound irradiation [28]. More interestingly, they even observed that reverse kebabs (crystal lamellae with uniform orientation along the long axis of nanofillers) were formed within carbon nanofibers [28]. To our knowledge, this is the first time that kebab structure is observed to form inside one-dimensional nanotubes rather than to be located on the outer surface to form the conventional nanohybrid shish-kebab structure [30,31]. Then, some unsolved questions appear. For instance, what

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is the difference between the formation mechanisms of the reverse and the conventional kebab structures? What factors affect the formation of the reverse kebab structure? These problems are difficult to answer based solely on experimental methods due to the limitations of observation scale.

Luckily, molecular simulation now becomes the third scientific method that is an effective complement to experimental and theoretical approaches. Up to now, both molecular dynamics (MD) simulations and dynamic Monte Carlo (MC) simulations have been successfully used to investigate polymer crystallization [19–21,32–40]. Hu and coworkers performed dynamic MC simulations of polymer crystallization confined in rigid nanotubes, and observed that polymer crystal orientation is controlled by interfacial interaction [20]. Previously, based on dynamic MC simulations, we systematically studied the crystallization behaviors of polymer nanocomposites, including the formation mechanism of the conventional nanohybrid shish-kebab structure [32,41], the crystallization of polymers grafted on substrates [35,42,43] and the synergic effects of chain orientation and nanotubes on polymer crystallization [33]. In the present paper, we applied dynamic MC simulations to investigate the molecular mechanism of kebab formation inside nanotubes in polymer solutions. It should be noted that in the simulations of Hu and coworkers, polymer melts were confined within a nanotube [20], while in our current simulations a nanotube was placed in polymer solutions. It was found that both the degree of confinement and the strength of interfacial interaction play important roles in the formation of the reverse kebabs. The increase of the strength of interfacial interaction and the decrease of lateral size can result in the rise of the degree of inside segmental orientation along the long axis of nanotubes, and thus the reverse kebab structure can be formed in the interior space.

2. Simulation details

Dynamic MC simulations of lattice model were used to study the polymer crystallization induced by a hollow nanotube in polymer solutions. We established a cubic lattice box with a size of $64 \times 64 \times 64$ lattice sites, and then put in a nanotube with a size of $49 \times V \times V$ lattice sites, as shown in Fig. 1 (V means that the lateral sizes along Y - and Z -axis directions were changed to study the effect of lateral size of nanotube on polymer crystallization). The long axis of the nanotube was parallel to the X -axis of the lattice box. Four lateral surfaces of the tube could not be passed through by polymer chains, while chains were allowed to pass into or out of the tube through both end surfaces. 3072 lattice chains, each containing 128 monomers, were put into the lattice box, and then polymer occupation density was 0.375 to mimic a polymer solution. The occupation density was defined as the ratio of the

number of lattice sites occupied by polymer segments to the number of total lattice sites. Thus, the corresponding polymer concentration was about 0.01 (the chain number/the box volume). In the lattice model, one monomer only occupied one lattice site. The bonds formed by two consecutive monomers could be oriented along lattice axes or along diagonals, and thus the coordination number of a monomer was just 26, corresponding to 6 axes, 8 body diagonals and 12 face diagonals. Monomers could move in the lattice box by jumping to their neighboring empty sites or sliding along local chain segments based on a micro-relaxation model [44]. In order to eliminate the finite size effect of the simulation box, periodic boundary conditions were introduced. The initial chains were then relaxed for 10^6 MC cycles to obtain amorphous random coils under athermal condition. The athermal condition corresponds to an infinitely high temperature, and each monomer has one chance to move during one MC cycle. Thus, in the current simulations, the number of MC cycles was used to reflect the simulation time. The random coils were then quenched to a low temperature for subsequent isothermal crystallization.

The conventional Metropolis sampling algorithm was used to decide monomer movements during micro-relaxation process according to the following potential energy penalty [44]

$$E = cE_c + pE_p + bB \quad (1)$$

where E_c is the energy change attributed to the connection of two non-collinear consecutive bonds, reflecting chain semi-flexibility, E_p is the energy change owing to each pair of nonparallel packed bonds, corresponding to the driving force for polymer crystallization, B is the energy change due to the presence of one monomer-nanotube pair, representing the strength of polymer-nanotube interaction, c is the net number of non-collinear connection pairs of bonds along the local chain, p is the net number of nonparallel packed pairs of bonds, and b is the net number of pair contacts between monomers and nanotube. In the simulation, the value of E_p/E_c was 1 so that chains have a proper flexibility at crystallization temperature, the value of B/E_c was varied from 0 to -0.5 to investigate the effect of interfacial interaction on polymer crystallization (the minus represents that attractive interaction exists between polymer and nanotube), and the reduced temperature kT/E_c (k is the Boltzmann's constant and T is the temperature) in the simulations was set to 2.7. For real systems, the interaction parameter between polymer chains and nanotube is mainly controlled by the chemical structure of the polymer and the surface structure of the nanotube. If both the polymer and the nanotube are non-polar, weak interfacial interaction exists between the polymer and the nanotube. However, high interfacial interaction exists between the polar polymer and the nanotube with polar surface structure.

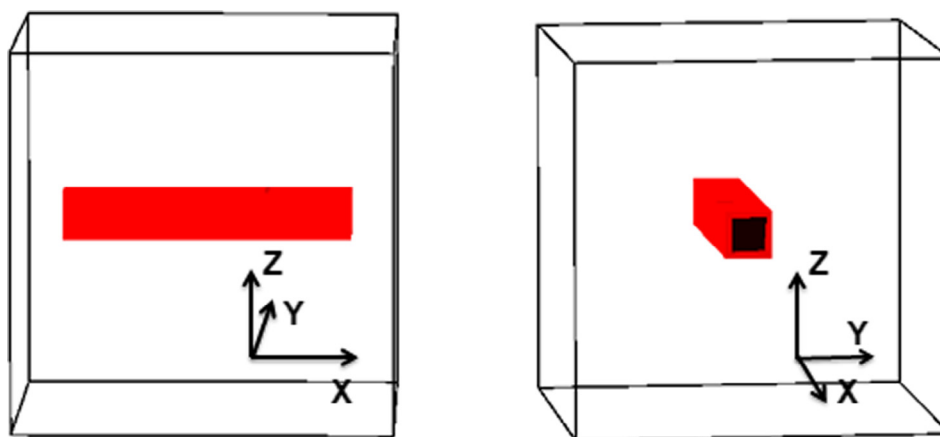


Fig. 1. Snapshots for the hollow nanotube with a lateral size of 6 lattice sites (red parts) observed along different directions, namely, (left) Y -axis and (right) X -axis directions, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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