Research Article

The Effect of Grafting Density on the Crystallization Behaviors of Polymer Chains Grafted onto One-Dimensional Nanorod

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The crystallization behaviors of five polymer chain systems grafted on a nanorod and the corresponding effect of grafting density were investigated by dynamic Monte Carlo simulations. The segment density near the interfacial regions, the number of crystallites, and the mean square radius of gyration \( <R_g^2> \) increase with increasing grafting density, which are beneficial to the enhancement of crystallizability. Meanwhile, the crystalline morphology is greatly influenced by grafting density and polymer-nanorod interaction. For the grafted system with 52 chains, a nanohybrid shish-kebab (NHSK) structure is formed, when the polymer-nanorod interaction \( (E_b/E_c) \) is -0.4. For the system with 128 chains, a NHSK structure is formed, when \( E_b/E_c \) is -1.0. For the system with 252 chains, NHSK structure cannot be formed. The findings in this work can supply important theoretical reference for the design, preparation, and application of polymer nanocomposites.

1. Introduction

It was previously reported that physical properties of composite materials, such as modulus, tensile strength and conductivity, can be dramatically improved by adding fillers into polymers [1–7]. Aluminium oxide, carbon nanotubes, silica particles, and graphene are the commonly used nanoscale fillers, which can significantly change crystalline morphologies of polymer nanocomposites, thus further leading to the improvements in mechanical properties [8–14]. It should be noted that the interaction between polymers and fillers is important for the crystallization of polymer nanocomposites [15, 16]. In general, if weak polymer-filler interaction exists between polymer and nanofillers, the dispersion of nanofillers and the mechanical properties of polymer nanocomposites will be poor [17]. Conversely, the relatively strong polymer-filler interaction can result in the good dispersion of nanofillers and also the excellent mechanical properties [18]. Thus, nowadays, researchers are trying to graft polymer chains onto fillers to enhance the polymer-filler interaction [19–23]. For instance, Yan et al. grafted polyamide 1010 on carbon nanotube and found that the dispersion of carbon nanotube is greatly improved [24]. Baek et al. prepared poly(phenylene sulfide)-graft-carbon nanotube and found that the electrical conductivity, dispersibility, and even melt-processability are improved [25]. Goh et al. grafted polyethylene on carbon nanotube and discovered that the mechanical properties of the corresponding nanocomposites are improved [26].

Nanofillers in polymer matrix can serve as the nucleating agents for polymer crystallization, which strengthen the nucleation ability [25–28]. Obviously, the crystallization process of grafted polymer systems can be affected because of the grafting points, which limit the motion of chain heads and influence the nucleation ability. Jana et al. [23] and Zhou et al. [29] explored the crystallization process of poly(ε-caprolactone)-grafted-carbon nanotubes. They both observed that carbon nanotubes cause the heterogeneous
nucleation of grafted polymer chains. Previously, we investigated the crystallization process of polymer chains graft on two-dimensional filler and observed that the heterogeneous nucleation does not happen with high grafting density under no polymer-filler interaction because of the crowding effect of grafted chains [30]. Moreover, some groups observed that the dimension of fillers seriously affects the crystalline morphology of polymers. For instance, Li et al. observed the appearance of the nanohybrid shish-kebab (NHSK) structure in experiments [31]. Zhou et al. studied the crystallization process of poly(ε-caprolactone)-graft-carbon nanotube but observed that no NHSK structure is formed [29].

In short, the presence of polymer chains grafted on nanofillers can dramatically change the crystallization behaviors of the corresponding polymers, resulting in the remarkable reinforcement effect. As a matter of fact, establishing the relationship between microscopic structures and macroscopic physical properties has always been one of the core tasks in the field of materials science. Thus, in order to prepare the high-performance polymer nanocomposites or effectively regulate physical properties of polymer nanocomposites, the microscopic mechanism of the crystallization of grafted polymers must be first revealed. However, up to now, few experimental studies on the microscopic mechanism of crystallization process for grafted polymers have been reported.

Luckily, computer simulations can supplement the short-comings of experimental and theoretical work in the investigation of crystallization process for grafted polymers, which can be further used to solve many basic problems raised in the field of polymer materials and also the important technical problems related to the processing of new polymer materials [32–36]. Many groups studied the crystallization behaviors of polymer systems by simulations [37–39]. In this work, we further explored the microscopic mechanism of crystallization process of polymers grafted on one-dimensional nanorod and investigated the effect of grafting density and polymer-nanorod interaction on the corresponding crystallization behaviors.

2. Simulation Details

Monte Carlo simulations [30, 32–36, 40–43] were employed to investigate the crystallization behaviors of grafted polymer systems. It should be noted that dynamic Monte Carlo simulation is a proven method for studying polymer crystallization. Hu et al. have used Monte Carlo simulations to study the different topics in crystallization behaviors of polymers, such as strain- or shear-induced polymer crystallization [40, 41], copolymer crystallization [44, 45], and chain-folding process in polymer crystallization [46]. Previously, our group also applied Monte Carlo simulations to uncover the microscopic mechanisms of crystallization behaviors in polymers [47–49]. A box with $64^3$ cubic lattice sites was constructed, and a one-dimensional nanorod with the length, width, and thickness being respective 64, 2 and 2 lattice sites was placed in the middle of the box, for which its long axis is along the $X$-axis, as exhibited in Figure 1(a). Then, polymer chains with 31 segments were grafted on the four lateral surfaces. Figure 1(b) shows a cross-section of the nanorod perpendicular to the $X$-axis. It can be seen that four typical grafted chains were grafted on the four lateral surfaces, and the green spheres represented the monomer units grafted directly on the nanorod. In order to explore the influence of grafting density on crystallization process, simulations were carried out for the systems with 52, 64, 84, 128, and 252 grafted polymer chains, respectively. Correspondingly, the grafted densities for the five systems are 0.10, 0.12, 0.16, 0.25, and 0.49. Figure 2 describes the position distributions of grafting points for the five systems with 52(a), 64(b), 84(c), 128(d), and 252(e) grafted polymer chains, respectively. For simplicity, only parts of the one-dimensional nanorod were drawn in Figure 2, and the dashed area represented the rest. During the simulation

![Figure 1](image-url)
process, one lattice can be occupied by only one segment or one lattice site of the nanorod. A bond connects by two nearby segments, which was oriented along lattice axes or diagonals. Accordingly, the coordination number of one segment site is twenty-six. The polymer chains can move on the basis of a microrelaxation model \[35, 36\]. In other words, one segment can jump from one lattice to an adjacent vacancy site or slide along the polymer chains. In addition, the segments that were directly grafted on the nanorod were not allowed to move during simulations. Furthermore, periodic boundary conditions were adopted.

The conventional metropolis sampling algorithm was employed in each step of microrelaxation with the potential energy penalty

$$\Delta E = \Delta c \cdot E_c + \Delta p \cdot E_p + \Delta b \cdot E_b$$  \(1\)

where \(E_c\) is the potential energy change owing to one noncollinear connection of continuous bonds along the chains, which can reflect the pliability of chains, \(E_p\) is the interaction energy parameter between two neighboring bonds, which represents the increase in energy caused by the nonparallel arrangements of two neighboring bonds \[50, 51\], \(E_b\) is the interfacial interaction energy between the nanorod and the nearest-neighbor segments \[44\], \(\Delta c\) and \(\Delta p\) are the numbers of changes of the corresponding noncollinear conformations and nonparallel arrangements of the neighboring bonds before and after sampling in simulations, and \(\Delta b\) is the net change of the nearest-neighbor segment-nanorod pairs. \(E_p/E_c\) was set to 1 \[32, 33\], and \(kT/E_c\) was denoted as the simulation temperature, which was further written as \(T^*\) in following sections. The ratio of polymer-nanorod interaction potential to noncollinear potential \((E_b/E_c)\) was set as 0, -0.1, -0.2, -0.3, -0.4, and -1.0 to explore the influences of polymer-nanorod interactions on the crystallization process of the systems.

The initial polymer chains were relaxed for \(10^6\) Monte Carlo (MC) cycles to obtain equilibrium amorphous state at an extremely high temperature. Here, one MC cycle denotes the step that all the monomers have one chance to move. As shown in Figure 3, after relaxation the polymer chains have evolved into the random coil state. Subsequently, the random coils were quenched into a simulation temperature \(T^* = 2.3\).

### 3. Results and Discussion

The influence of grafting density on the crystallization behaviors of grafted polymer systems without polymer-nanorod interaction was first studied. Figure 4 reveals the evolutions of crystallinity of five systems with different grafting densities during isothermal crystallization process. The definition of crystallinity is the proportion of crystalline bonds (the bonds have more than five parallel neighbors) in all bonds. As shown in Figure 4, after the nucleation induction period (during which the corresponding crystallinity is nearly zero), the values of crystallinity rise immediately and then tend to be stable. In addition, the systems with higher grafting densities have the higher final crystallinity. For the grafted systems...
Figure 3: Relaxed polymer systems with 52(a), 64(b), 84(c), 128(d), and 252(e) polymer chains. Blue cylinders denote the polymer chains, and red parts represent the nanorod.

Figure 4: Evolutions of crystallinity for five systems with different grafting densities during isothermal crystallization process, respectively.

system with 52 polymer chains, the crystallinity is almost zero, indicating that crystallization did not occur in this system. It also can be clearly seen that, with increasing grafting density, the nucleation induction period of the grafted polymer system becomes shorter. Zhou et al. prepared poly(ε-caprolactone)-graft-carbon nanotubes and observed that larger nucleation effect exists in the polymers with higher grafting densities [50]. Moreover, the higher grafting density leads to higher final crystallinity for the grafted systems [50]. These conclusions are in accordance with our simulation results. The increase of grafting density can cause the increase of the number of segments. Then, in higher grafting density systems, more crystal nuclei can appear during crystal nucleation, and more segments can take part in the subsequent process of crystal growth, resulting in higher final crystallinity. In the following sections, we focus on the microscopic structure changes of polymer chains during crystallization process for different grafted systems.

The density of segments in interfacial regions can affect polymer crystallization process. Here, the interfacial regions are treated as the first layers next to the nanorod, and the definition of segment density near the surface regions is the ratio of the segment number near the surface regions to the total number of lattice sites near the surface layers. For the blend system of ungrafted polymers and nanorod, the nanorod may limit the conformations of polymer chains near the nanorod surface, causing the conformational entropy reduction. As a result, the segments in the vicinity of the filler surface will be inclined to move towards the exterior zone, leading to the reduction of segment density in the interfacial regions. However, the emergence of this situation can be avoided in the grafted systems. The segment motions of the grafted chains are forcibly restrained by the grafting points, which prevent the grafted chains moving away from the filler surface. Figure 5 shows the segment density near the surface regions of the systems with 52, 64, 84, 128,
Figure 5: Segment density near the nanorod for the grafted polymer systems with 52, 64, 84, 128, and 252 polymer chains, respectively.

and 252 polymer chains, respectively. The segment density increases with increasing chain numbers. In general, the systems with higher segment density usually have higher degree of supercooling and higher melting points. Then, the critical free energy barrier of nucleation is lower [51]. In other words, the ability of nucleation for the systems with higher chain numbers can be enhanced, leading to the shorter nucleation periods, as shown in Figure 4. Similar phenomena were also observed in experiments for the polymers grafted on graphene [52] and carbon nanotubes [21].

Chain conformation can also influence polymer crystal nucleation process in the light of the classic crystal nucleation theory [51, 53]. The existence of grafting points induces the conformation changes of grafted polymer chains. The parameter, mean square radius of gyration ($<R_g^2>$), can describe the conformations of polymer chains. Figure 6 shows $<R_g^2>$ of the five relaxed systems before the crystallization process, respectively. Although the length of the polymer chains is identical, the $<R_g^2>$ still increases with increasing grafting density, implying that the chain conformations are more extended with higher grafted density owing to the stronger crowded effect. Xu et al. studied poly($\varepsilon$-caprolactone)-g-carbon nanotube with high grafting density and indeed found that grafted polymer chains are overcrowding and highly extended [50]. The crowding effect leads to the loss of conformational entropy and the increase of melting points. For the sake of uncover the influence of grafting density on the melting point, the evolutions of crystallinity for the grafted polymer systems with 64, 84, 128, and 252 polymer chains during heating processes were shown in Figure 7. In order to get the melting temperature, the equilibrium melts of the four grafted systems were cooled with the cooling rate of 0.01 unit of $T^*_m$ per 500 MC cycles from $T^*_m = 5.0$ to 1.0. After that, the systems were heated from $T^*_m = 1.0$ to 5.0. In Figure 7, the melting temperature ($T_{m}$) is the temperature when the crystallinity is zero. It is shown that the melting temperatures increase with the increase of grafted density. In brief, the increase of the grafting density causes the significant improvement in melting temperatures, demonstrating that the thermodynamic effect occupies the dominant position.

Figure 8(a) shows the respective initial crystal morphologies of the systems with 64, 84, 128 and 252 polymer chains,
respectively. For the four systems, the initial crystalline stems are inclined to be perpendicular to the long axis of the nanorod. Figure 8(b) demonstrates the corresponding crystalline morphologies at 300000 MC cycles. The initial small crystallites gradually grow into large crystals. It is shown that the crystalline stems in the system with 64 chains (low grafting density) are oriented perpendicular to the long axis of the nanorod. As the grafting density increases, the number of the crystals increases, indicating that more segments can participate in the crystallization. Thus, the systems with higher grafting density have the higher ultimate crystallinity, as shown in Figure 4. Furthermore, the crystals in the systems with high grafting density (128 and 252 chains) exhibit different orientations, but no orientation of crystalline stems along the long axis of the nanorod can be observed. These phenomena can be attributed to the small lateral size of the nanorod and the distributions of the grafting points. As shown in Figure 2, the grafting points are aligned along the long axis of the nanorod, and then the arrangement of segments along the long axis of the nanorod will be hindered owing to the crowding effect. Thus, no crystalline stems oriented along the long axis can be observed in these grafted systems. Furthermore, to uncover the influence of the polymer-nanorod interaction, the crystalline morphologies at 300000 MC cycles for three grafted polymer systems containing 52, 128, and 252 chains with the specified polymer-nanorod interaction were shown in Figure 9. For the grafted polymer system with 52 chains (Figure 9(a)), crystallization does not take place, when no interfacial interaction exists ($E_b/E_c = 0$). Crystallites appear in the systems with larger interfacial interactions ($E_b/E_c = -0.1, -0.2, -0.3, -0.4$, and $-1.0$), indicating that the improvement of the polymer-nanorod interaction is beneficial to the crystallization of the grafted polymers. In addition, increasing the polymer-nanorod interaction can lead to the changes of the crystalline morphology. When the value of $E_b/E_c$ is -0.2 or -0.3, the crystalline stems in some crystals start to orient along the long axis of the nanorod. When polymer-nanorod interaction was further increased to $E_b/E_c = -0.4$ and -1.0, all the crystalline stems exhibit uniform orientation along the long axis of the nanorod, and the typical NHSK structure appears.

However, the influence of polymer-nanorod interaction on crystalline morphologies for the systems with 128 chains is somewhat different from that for the systems with 52 chains. As shown in Figure 9(b), the crystalline stems tend to be perpendicular to the long axis of the nanorod, when $E_b/E_c$ is 0. When $E_b/E_c$ is -0.1, -0.2, -0.3, and -0.4 (higher polymer-nanorod interactions), the crystalline stems in some crystals begin to arrange parallel to the long axis of the nanorod. All crystals show uniform orientation along the long axis of the
Figure 9: The crystalline morphologies on 300000 Monte Carlo cycles of three systems for 52(a), 128(b) and 252(c) polymer chains with the polymer-nanorod interactions of 0(a)–(c)(A), -0.1(a)–(c)(B), -0.2 (a)–(c)(C), -0.3 (a)–(c)(D), -0.4 (a)–(c)(E), and -1.0 (a)–(c)(F). Yellow cylinders represent for the crystalline stems and the red parts denote the nanotubes.

nanorod (NHSK structure appears), when the value of $E_b/E_c$ is -1.0. In other words, the NHSK structure in the system with higher grafting density is formed under higher polymer-nanorod interaction.

For the system with 252 polymer chains (Figure 9(c)), no perfect NHSK structure is formed in all the conditions with different polymer-nanorod interactions. This phenomenon can be attributed to the very high grafting density and strong crowding effect. Owing to the strong crowding effect, the chains are forced to "stand" on the nanorod surfaces, the orientation of which tends to be perpendicular to the long axis of the nanorod, as revealed by the largest value of $\langle R_g^2 \rangle$ of the systems with 252 chains in Figure 6. In experiments, the perfect NHSK structures were observed mainly in polymer/nanorod blend systems. This is the first time that the NHSK structure is observed in the grafted polymer systems. The NHSK structure can only appear with the appropriate grafting density and relatively high polymer-nanorod interaction.

The current simulation results reveal that the crystalline morphology in polymers grafted on one-dimensional nanofiller can be regulated by changing the grafting density and interfacial interaction. Apparently, these systems with different crystalline morphologies should exhibit different physical properties. Thus, we believe that the current findings can provide some guidance for the design and manufacture of new high-performance polymer nanocomposites.

4. Conclusion

The crystallization process of polymer chains grafted onto a nanorod is different from those of the polymer/nanofiller blend system. As the grafting density increases, the nucleation ability and the final crystallinity can be greatly improved. The segment density near the nanorod, the number of crystallites, and the $\langle R_g^2 \rangle$ of relaxed polymer chains increase with increasing grafting density, which are beneficial to the enhancement of crystallization ability. Meanwhile, the crystalline morphology is also significantly influenced by grafting density and polymer-nanorod interaction. For the grafted system with 52 chains, the NHSK structure appears when the value of $E_b/E_c$ is -0.4. However, the NHSK structure is formed for the grafted system with 128 chains, when the value of $E_b/E_c$ is -1.0. The perfect NHSK structure could not appear in the grafted system of 252 chains under the specified polymer-nanorod interaction owing to the excessively
high grafting density and strong crowding effect. Thus, the formation of NHSK structure requires appropriate grafting density and relatively high polymer-nanorod interaction. This work is helpful for the understanding of the mechanism of crystallization process of grafted systems and can provide some guidance for the design of high-performance polymer composites with the NHSK structure.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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