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Differences in Crystallization Behaviors between Cyclic and Linear Polymer Nanocomposites

Rong-Juan Liu^a, Zhi-Ping Zhou^{a*}, Yong Liu^a, Zhao-Peng Liang^a, Yong-Qiang Ming^a, Tong-Fan Hao^b, and Yi-Jing Nie^{a*}

^a Research School of Polymeric Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

^b Institute of Green Chemistry and Chemical Technology, Jiangsu University, Zhenjiang 212013, China

Abstract Cyclic polymers exhibit fascinating crystallization behaviors owing to the absence of chain ends and more compact conformations. In the current simulation, dynamic Monte Carlo simulations were performed to reveal the underlying mechanism of the effect of chain topology and chain length on crystallization of polymer in solutions containing one-dimensional nanofiller. Simulation results suggested that the filled cyclic polymers exhibit higher melting temperature, higher crystallization temperature, and faster crystallization rate than the analogous linear polymers of identical chain length, especially in the systems with relatively short chains. Based on the Thomson-Gibbs equation, we theoretically analyzed the difference in the melting point between the cyclic and linear polymers under different chain lengths, and derived the dependence of the ratio of the melting point of the linear polymers to that of its cyclic analogs on chain length. In addition, it was also observed that the nanofiller can induce the formation of nanohybrid shish-kebab structure during isothermal crystallization of all systems.

Keywords Cyclic polymers; Linear polymers; Crystallization

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INTRODUCTION

In recent years, cyclic polymers have attracted widespread attention due to the lack of free chain ends. This topological singularity can result in significant differences in crystallization behaviors of cyclic polymers and linear analogs, further affecting both microscopic structures and macroscopic physical properties of polymers.^[1–3] Thus, the detailed crystallization process of cyclic polymers should be investigated to understand the effect of chain topology on polymer crystallization.

The complex crystallization behavior of cyclic polymers is a fundamental subject in polymer science. Until now, investigations on cyclic polymers and linear analogs have been extensively carried out and some controversial results have been reported.^[4–19] Previously, Pérez *et al.* observed that cyclic poly(ϵ -caprolactone) (PCL) exhibits higher nucleation rate and higher crystallization rate at any given crystallization temperatures compared to analog linear PCL.^[10] Similar phenomenon was also found by Zardalidis *et al.* for cyclic and linear poly(oxyethylene) (POE), in which cyclic POE crystallizes faster than analog linear POE.^[11] Based on molecular dynamics (MD) simulations, Sommer and coworkers also observed that the stem length and the final crystallinity of cyclic polymers are

substantially higher than those of the analog linear polymers.^[12] In contrast, it has also been reported that cyclic poly(tetrahydrofuran) (PTHF) crystallizes more slowly than its linear counterparts.^[13] This conflicting phenomenon also exists in melting temperature and lamellar thickness. For instance, Shin and coworkers observed that the values of melting temperature and lamellar thickness of cyclic poly(L-lactide) (PLLA) both are larger than those of linear PLLA.^[14] However, completely opposite results have been reported by Tezuka and Sugai.^[13,15] Iyer and Muthukumar also found that cyclic polymers melt at a lower temperature compared to linear counterparts.^[16] These contrastive behaviors between cyclic polymer melts and linear polymer melts have been discussed from the following two viewpoints: kinetic factors controlled by diffusion and thermodynamic factors determined by different supercooling.^[1,17,18] Nevertheless, some ambiguities still exist in the crystallization behavior of cyclic polymers, and more research efforts are needed.

As we know, the incorporation of nanofillers into polymers can significantly affect crystallization behaviors of polymers, thus affording polymer nanocomposites with excellent mechanical properties.^[20–22] In general, the addition of nanofillers with an appropriate amount and optimum size can accelerate heterogeneous nucleation of polymer chains on filler surface and eventually induce the formation of various crystalline structures.^[23–33] For example, nanohybrid shish-kebab (NHSK) structures initiated by one-dimensional nanofillers have been detected in several filled systems, such as homo-

* Corresponding authors, E-mail: zhouzp@ujs.edu.cn (Z.P.Z.)

E-mail: nieyijing@ujs.edu.cn (Y.J.N.)

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polymers, random copolymers, and block copolymers.^[30–33] Furthermore, crystallization behaviors of cyclic polymers are also changed with the addition of nanofillers.^[34,35] Previously, a nucleating effect has been found in cyclic PCL systems incorporated by single-wall carbon nanotubes functionalized with octadecylamine (SWNT-ODA).^[34] Besides, it has also been observed that the addition of graphene oxide nanoplatelets (rGON) in cyclic ultrahigh-molecular-weight polyethylene (UHMWPE) facilitates the formation of crystals with high melting temperature.^[35] However, so far, only a few works on cyclic polymer nanocomposites have been reported, which inspires us to further investigate the crystallization behaviors of cyclic polymers filled with nanofillers.

By means of dynamic Monte Carlo (MC) simulations, our group have investigated crystallization behaviors of various systems under different conditions.^[36–43] However, these previous works focused only on linear polymer systems, while cyclic polymer systems may show some new and interesting phenomena. In the current simulation, we concentrate on the investigation of the difference in crystallization behaviors between cyclic polymer nanocomposites and analog linear polymer nanocomposites. In addition, the effects of molecular chain length on crystallization behaviors of cyclic polymers and linear polymers are also considered. Our simulation results show that in the systems with shorter chains, the filled cyclic polymers exhibit higher melting points and crystallization rates compared with the analog linear polymers, while in the systems with relatively long chains, those differences become less pronounced. To further analyze these phenomena theoretically, we deduce the cyclization entropy difference between the cyclic and linear polymers as a function of chain length, and establish the relationship between the melting point of the cyclic polymers and that of its linear analogs under different chain lengths, which fits our simulation data very well. Furthermore, NHSK structures induced by the nanofiller can form in all systems with various chain lengths and diverse chain topologies, while the lamellar thickness of each system is essentially different.

SIMULATION DETAILS

Current dynamic MC simulations are carried out in a cubic lattice box with periodic boundary conditions, and the coarse-grained model of polymer chains is employed. In this case, each lattice site is only allowed to be occupied by one polymer bead (one polymer bead is regarded as one monomer in the following parts). Namely, double occupation of one site by different beads and bonds crossing of different chains both are forbidden. Since polymer bonds might orient along the lattice axes, the plane diagonals and the body diagonals of the lattice box, the coordination number of each lattice site could be counted as 26.^[44] In the simulation, we distinguish the cyclic polymer chains and the linear polymer chains by limiting the distance between the 1st monomer and the N^{th} monomer of a cyclic chain within the length of one bond, as illustrated in Fig. 1. Thus, for the pre-placed chains, a linear polymer chain is fully extended while a cyclic polymer chain is semi-extended due to the structural limitation. At first, regularly arranged polymer chains (denoted by a set of monomers connected by bonds) and one-dimensional nanofiller (represented by a strip with the size of $64 \times 1 \times$

1) are placed in the cubic lattice space with the side length of 64 lattice sites, as depicted in Fig. 2. To maintain the occupation density of polymer chains of 0.125 to simulate dilute solution systems, chain length (N) is varied from 8, 32, 64, and 128 to 256 lattice sites, corresponding to the systems with chain number of 4096, 1024, 512, 256, and 128, respectively. Since the snapshots of initial states for the cyclic polymers and the linear polymers are similar, Fig. 2 only displays the corresponding states for the cyclic polymers with different chain lengths. To help readers understand the initial state of the cyclic polymers more clearly, a cyclic polymer chain in the system with $N = 64$ is taken as an example and partially enlarged, as shown in the inset (a) of Fig. 2.

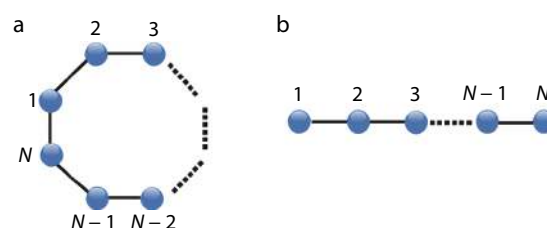


Fig. 1 Illustration of (a) one cyclic polymer chain and (b) one linear polymer chain. Here, the blue spheres denote the monomers in corresponding chains.

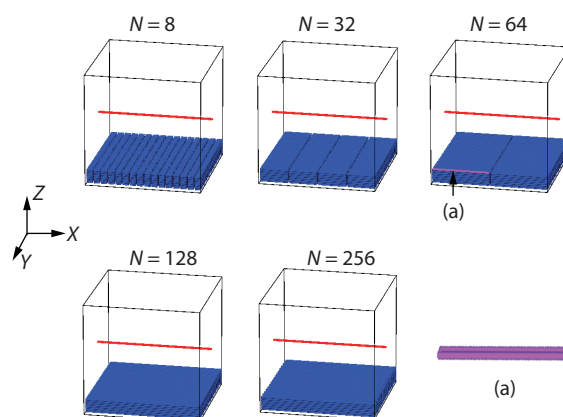


Fig. 2 Snapshots of initial chains for the filled cyclic polymers with different chain lengths. The blue cylinders and the red strip stand for the polymer bonds and the one-dimensional nanofiller, respectively. To help readers understand the initial state of the cyclic polymers more clearly, a cyclic polymer chain (represented by the purple cylinders) in the system with $N = 64$ is taken as an example and partially enlarged, as shown in the inset (a).

In the dynamic on-lattice MC simulations, polymer chains move on lattice space according to a micro-relaxation model, including one-site displacement and local sliding diffusion.^[45] This motion mode increases the rate at which the polymers can sample configuration space and mimics the real dynamics of polymers. For this reason, this micro-relaxation model allows us to gain some insights into the dynamics by which an initial nonequilibrium state of the polymer system relaxes.^[45] The conventional Metropolis sampling algorithm is employed to determine if an attempted motion can be accepted, and the corresponding potential energy change pro-

duced by an attempted motion can be calculated by the following equation:

$$\Delta E = \Delta c E_c + \Delta p E_p + \Delta b B + \sum_i f_i E_f \quad (1)$$

where E_c is the energy variation caused by two consecutive bonds that are not collinearly connected, E_p represents the energy variation caused by two adjacent bonds that are non-parallel packed, B reflects the energy variation caused by one monomer-filler pair, E_f denotes the energy barrier due to each pair of parallel-arranged bonds existing in the sliding path of one bond, Δc , Δp , and Δb correspond to the net changes in the number of non-trans conformation, nonparallel packed pairs of adjacent bonds, and monomer-filler pairs, respectively, and $\sum_i f_i$ is the total number of parallel packed bonds along the route of local sliding diffusion.^[46] Then, the acceptance probability of the new conformation obtained after an attempted motion can be expressed as follows:

$$p = \min \{1, \exp(-\Delta E/kT)\} \quad (2)$$

where k is the Boltzmann's constant and T is the simulation temperature. If the energy of the new conformation is lower than the energy of the original conformation, the new conformation will be accepted. Conversely, if the energy of the new conformation is higher than the energy of the original conformation, the program will generate a random number in the range $[0, 1]$ and compare it with the Boltzmann factor $\exp(-E/kT)$. In this case, if the value of the random number is larger, the new conformation will be rejected, otherwise the new conformation will be accepted. In the simulation, each monomer has an opportunity to try to move in one MC cycle. Therefore, we treat MC cycle as the time unit, and the total number of MC cycles as the simulation time. In addition, the potential energy barrier can be represented by the reduced parameters. In the current research, the values of E_p/E_c and E_f/E_c are fixed as 1 and 0.02 to ensure a proper flexibility and a strong mobility for polymer chains, B/E_c is set as -1 to allow attractively interfacial interaction existing between polymer chains and nanofiller, and the reduced temperature kT/E_c is simplified as T in this article.

With the help of the micro-relaxation motion model, the pre-placed polymer chains are relaxed into random coils under the non-thermal state. The mean square radius of gyration $\langle R_g^2 \rangle$ is calculated to ensure that the equilibrium state has been reached, as shown in Table 1. It has been found that the components of $\langle R_g^2 \rangle$ along X-axis, Y-axis, and Z-axis are approximately the same, indicating that all the systems in the current simulation are equilibrated after the relaxation process. Afterward, cooling and subsequent heating programs are performed to investigate the crystallization and melting behaviors of the cyclic polymers with different chain lengths and also the analogous linear polymers. Simulations of isothermal crystallization are also carried out to reveal the crystallization mechanism of different systems. It should be noted that each set of data in the entire paper is averaged over three independent simulations, which improves the accuracy and reliability of our results.

RESULTS AND DISCUSSION

Fig. 3 depicts the crystallinity evolutions for the cyclic polymers

Table 1 The values of the components of $\langle R_g^2 \rangle$ along X-axis, Y-axis, and Z-axis for the filled cyclic and linear polymers under the equilibrium state.

		$\langle R_g^2 \rangle$ along X-axis	$\langle R_g^2 \rangle$ along Y-axis	$\langle R_g^2 \rangle$ along Z-axis
Cyclic polymer	$N = 8$	0.98113	0.97366	0.99641
	$N = 32$	2.75186	2.68637	2.85062
	$N = 64$	5.22528	5.37225	5.51161
	$N = 128$	11.43576	11.39355	11.92065
	$N = 256$	21.65253	21.83041	21.15353
Linear polymer	$N = 8$	1.43280	1.45911	1.49615
	$N = 32$	5.12091	5.22274	5.44783
	$N = 64$	10.62756	10.75757	10.53476
	$N = 128$	23.25400	23.53528	23.83262
	$N = 256$	49.89807	50.29529	49.96426

and the analogous linear polymers under different conditions in the cooling-heating process. As defined in our previous work, the crystallization temperature (T_c) is regarded as the temperature at which the crystallinity curve begins to rise during cooling, and the melting temperature (T_m) is regarded as the temperature at which the crystallinity curve no longer decreases during heating.^[31,32] Thus, T_c and T_m both can be obtained from the intersections of the transition curves and the horizontal curves, as marked by arrows in Fig. 3(a). It should be emphasized that the kinetic estimates of T_c and T_m of all the simulated systems are provided in the current simulation, rather than the equilibrium crystallization temperature and the equilibrium melting temperature. Furthermore, crystallinity is considered as the ratio of the number of crystalline bonds to the total number of polymer bonds in these filled systems. Here, we treat a crystalline bond as a bond surrounded by at least five parallel-arranged bonds in the nearest-neighbor regions, and conversely, this bond will be treated as an amorphous bond. In analogy to experimental measurements based on differential scanning calorimetry (DSC), we stepwise reduce the temperature from $T = 5.00$ to 0.01 with a step length of 0.01 temperature unit and a step period of 500 MC cycles in the cooling process, and then improve the temperature back to $T = 5.00$ with the same rate in the heating process. Figs. 3(a) and 3(b) depict the variations of crystallinity curves for the cyclic polymers with different chain lengths and the analogous linear polymers during the cooling-heating programs, respectively. It can be obviously seen that the crystallinity evolution curves for these corresponding systems exhibit typical hysteresis between the cooling and heating processes, indicating nucleation-controlled first-order phase transition on cooling. In addition, it seems that both T_c and T_m of the cyclic polymers and linear polymers increase as the chain length increases. To more clearly describe the dependence of T_c and T_m on chain length and chain topology shown in Figs. 3(a) and 3(b), Fig. 4 further plots the variations of T_c and T_m for the filled cyclic and linear polymers as a function of chain length. As depicted in Fig. 4(a), as the chain length increases, T_c of both cyclic polymers and linear polymers grows up rapidly at first and then saturates at the high molecular weights. Similar tendency can also be observed in Fig. 4(b), which displays the dependence of T_m of the cyclic polymers and linear polymers on chain length. This relationship between T_m and chain length has been confirmed in both experiments and simulations.^[45,47] Previously, considering

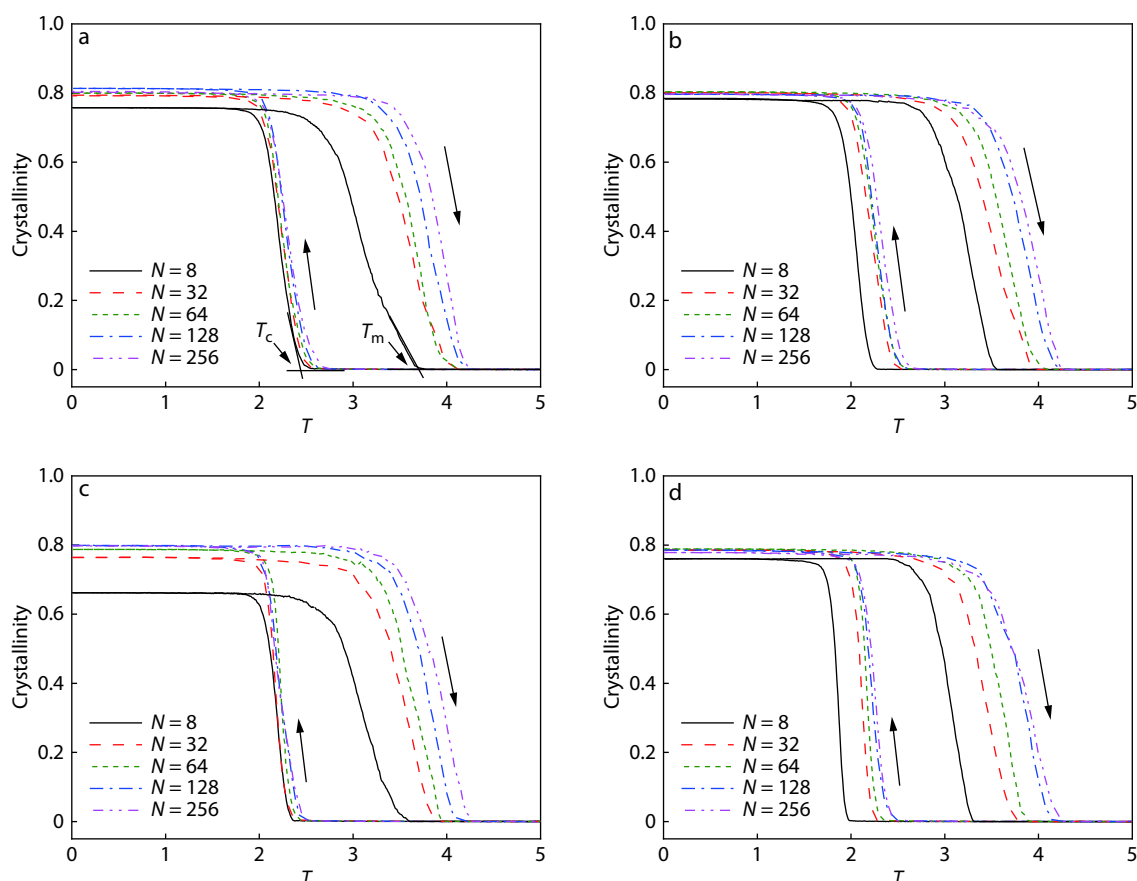


Fig. 3 Crystallinity curves as a function of temperature for (a) the filled cyclic polymers and (b) the filled linear polymers during cooling-heating program. Crystallinity curves as a function of temperature for (c) the unfilled cyclic polymers and (d) the unfilled linear polymers during cooling-heating program.

the free energy contribution of chain ends of linear polymers, Flory and Vrij derived the Flory-Vrij equation and suggested that chain ends can act as lattice defects to decrease the value of T_m .^[48,49] Hence, the linear systems with shorter chains generally exhibit lower T_m due to more chain ends in them, while T_m of the linear systems with relatively long chains is almost unchanged since in this condition the free energy contribution of chain ends is not significant. Furthermore, under this condition, shorter linear chains experience lower degree of supercooling and higher nucleation barrier, leading to lower values of T_c .^[10,50] Nevertheless, since the value of T_m for longer linear chains is irrespective of chain length, the degree of supercooling becomes insensitive to chain length and the saturated values of T_c can be obtained in systems with longer chains. For the cyclic polymers without chain ends, shorter chains consist of fewer segments and these segments between different chains are not related. Thus, compared to the cyclic systems with longer chains at the same density, the cyclic systems with shorter chains have more chain conformations, resulting in higher conformational entropy and lower values of T_m . However, since the conformation of longer cyclic chains is similar to that of linear chains, T_m of the cyclic polymers is also independent of chain length when chains are relatively long. In addition, the dependence of T_c of the cyclic polymers on chain length can also be attributed to the change in degree of

supercooling caused by the altered T_m with increasing chain length. Previously, it has been found that both the values of T_c and T_m of melt systems decrease with the increase of molecular weight at very high molecular weight values, which can be attributed to the onset of diffusion control as the entanglement molecular weight is reached and exceeded.^[17] Nevertheless, since our current systems simulate solution systems, the effect of entanglement can be negligible. Therefore, in the current simulation, for the systems with relatively long molecular chains, the values of T_c and T_m both seem to be independent of chain length. Another significant trend observed in Fig. 4 is that all cyclic polymer systems exhibit higher T_c and T_m compared with the analogous linear polymer systems with same chain lengths, which has also been observed in cyclic PCL and its linear counterparts.^[17] Compared to the linear chains, the cyclic chains of identical chain length display smaller conformational entropy due to the lack of chain ends, thus exhibiting larger value of T_m . However, since such end-group effect is weakened for longer linear chains, the difference in T_m between the cyclic polymers and the linear polymers becomes small in the systems with relatively long polymer chains. Furthermore, the higher T_m of cyclic polymers can result in larger degree of supercooling and lower nucleation barrier. Thus, the value of T_c of the cyclic polymers is also larger than that of the linear counterparts of identical chain length. In the systems with relatively long

polymer chains, as the degree of supercooling of the cyclic polymers and linear polymers is getting closer with increasing chain length, the difference in T_c between the cyclic polymers and corresponding linear polymers is reduced.

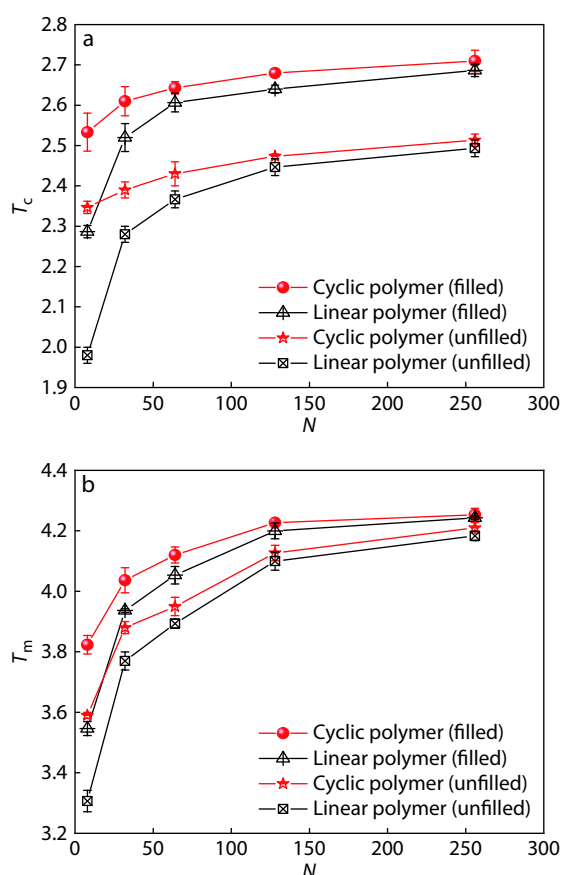


Fig. 4 (a) Variations of T_c for the filled/unfilled cyclic polymers and analogous linear polymers as a function of chain length. (b) Variations of T_m for the filled/unfilled cyclic polymers and analogous linear polymers as a function of chain length. The error bars are obtained from three independent simulations of parallel systems (the same in the following figures).

We further perform cooling and subsequent heating programs for the corresponding systems without nanofiller to reveal the role of nanofiller on the crystallization and melting behaviors. As depicted in Figs. 3(c) and 3(d), in the systems without nanofiller, T_c and T_m are still dependent on chain length and chain topology, which is consistent with the simulation results of the filled systems. However, compared to the systems filled with nanofiller in Figs. 3(a) and 3(b), the values of T_c and T_m for the corresponding systems without nanofiller in Figs. 3(c) and 3(d) seem to be lower. The variations of T_c and T_m for the corresponding systems without nanofiller are more clearly illustrated in Fig. 4. It can be seen that the presence of nanofiller can increase T_c and T_m in both the cyclic polymers and the linear polymers. The increased T_c can be attributed to the reduction in the nucleation barrier caused by heterogeneous nucleation on the nanofiller surface. Furthermore, in the systems filled with nanofiller, the nanofiller in-

duces polymer chains to crystallize to form lamellar crystals, which are more perfect than the crystals formed in the systems without nanofiller. Thus, these filled systems exhibit higher T_m .

To more clearly reveal the difference in crystallization and melting behaviors between the cyclic polymers and the analogous linear polymers, we further theoretically analyze T_m of these corresponding systems. It should be noted that in the following theoretical analysis, we ignore the influence of nanofiller and only discuss the role of chain topology and chain length. According to the well-known Thomson-Gibbs equation, T_m for linear polymers is given by:^[1,3]

$$T_{mL} = T_{mL}^0 \left[1 - \frac{2\sigma_e}{\Delta h_f^0 l} \right] \quad (3)$$

where T_{mL} is the melting temperature of the linear polymers obtained in the current simulation (which is related to the degree of perfection of crystals formed during crystallization), T_{mL}^0 is the equilibrium melting temperature of the linear polymers (which refers to the melting temperature at which the crystal thickness is infinite), σ_e is the fold surface free energy, Δh_f^0 is the difference in equilibrium melting enthalpy, and l is the lamellar thickness. In order to more clearly describe the difference in free energy between the cyclic polymers and its linear counterpart, Su *et al.* introduced a “cyclization free energy” to modify the Hoffman-Weeks and Thomson-Gibbs equations for the cyclic polymers.^[3] The modified Thomson-Gibbs equation for the cyclic polymers can be expressed as follows:^[1,3]

$$T_{mC} = \frac{T_{mL}^0}{\left(1 + \frac{T_{mL}^0 \Delta S_{cyc}}{\Delta h_f^0} \right)} \left[1 - \frac{2\sigma_e}{\Delta h_f^0 l} \right] \quad (4)$$

where T_{mC} is the melting temperature of the cyclic polymers obtained in the current simulation, ΔS_{cyc} is the cyclization entropy difference between the cyclic and linear polymers, which is susceptible to chain length. Due to the absence of chain ends and more compact molecular conformations of the cyclic polymers, the value of ΔS_{cyc} should be negative. According to Eqs. (3) and (4), the relationship between T_{mC} and T_{mL} can be deduced as follows:

$$\frac{T_{mL}}{T_{mC}} = \left(1 + \frac{T_{mL}^0 \Delta S_{cyc}}{\Delta h_f^0} \right) \quad (5)$$

In fact, ΔS_{cyc} can be calculated from the difference between the entropy of the cyclic polymers and that of their linear counterparts. Thus, we further deduce ΔS_{cyc} in the current simulations. According to the random walk model, we assume that one end of the polymer chain is fixed at the origin A , and the other end reaches the position B after N steps.^[51] Therefore, for a linear polymer chain, the total number of random walks (W_L) can be given by:

$$W_L = (z - 1)^N \quad (6)$$

where z is the coordination number of the lattice.

Different from linear polymer chains, the position B at which the end of cyclic polymer chains arrives after N steps should be limited to the nearest lattice sites of the origin A . Namely, the end-to-end distance (L ; the distance from the 1st

monomer to the N^{th} monomer) of a cyclic polymer chain in the lattice space should not be larger than the maximum value of the length of one bond (l). The coordination number of each lattice site is 26 as described above, and then the probability distribution of the position B for a cyclic polymer chain can be calculated:

$$P(\mathbf{L}, N) = 26 \left(\frac{3}{2\pi N l^2} \right)^{3/2} \exp \left(-\frac{3\mathbf{L}^2}{2N l^2} \right) \quad (7)$$

Here, we set the length of each bond (including the bond connecting the 1st monomer and the N^{th} monomer) as 1 lattice sites for simplicity. Then, Eq. (7) can be simplified as follows:

$$P(\mathbf{L}, N) = 26 \left(\frac{3}{2\pi N} \right)^{3/2} \exp \left(-\frac{3}{2N} \right) \ll 1 \quad (8)$$

Thus, for a cyclic polymer chain, the total number of random walks (W_C) can be given by Eq. (9), which is less than the value of W_L .

$$W_C = (z-1)^N P(\mathbf{L}, N) = 26(z-1)^N \left(\frac{3}{2\pi N} \right)^{3/2} \exp \left(-\frac{3}{2N} \right) \quad (9)$$

In the current simulation, we keep a constant total number of monomers (Q ; the product of the number of monomers contained in each chain and the number of chains contained in each system) to ensure the same density for each system. Hence, the number of chains contained in each system can be expressed as Q/N . Further, the cyclization entropy difference between cyclic polymer systems containing Q/N polymer chains and their analog linear polymer systems of identical chain length can be calculated by:

$$\Delta S_{\text{cyc}} = \frac{Q}{N} k (\ln W_C - \ln W_L) = \frac{Q}{N} k \ln \left(26 \left(\frac{3}{2\pi N} \right)^{3/2} \exp \left(-\frac{3}{2N} \right) \right) \quad (10)$$

where k is the Boltzmann's constant. Since the value of W_C is less than W_L , we can conclude that $\Delta S_{\text{cyc}} < 0$, which is consistent with theoretical analysis. Then, we replace $\ln \left(26 \left(\frac{3}{2\pi} \right)^{3/2} \right)$ with constant C for simplicity, and hence Eq. (10) can be simplified into

$$\Delta S_{\text{cyc}} = \frac{Qk}{N} \left(C - \frac{3 \ln N}{2} - \frac{3}{2N} \right) \quad (11)$$

Substituting Eq. (11) into Eq. (5), we have

$$\frac{T_{\text{mL}}}{T_{\text{mC}}} = \left[1 + \frac{T_{\text{mL}}^0 Qk}{\Delta h_f^0 N} \left(C - \frac{3 \ln N}{2} - \frac{3}{2N} \right) \right] \quad (12)$$

Eq. (12) establishes the relationship between the melting point of cyclic polymers and that of its linear analog with different chain lengths on the condition that the effect of nanofiller is neglected. According to Eqs. (10) and (11), the values of ΔS_{cyc} of the systems with chain length of 8, 32, 64, 128, and 256 can be calculated as $-4737.69 \times k$, $-3169.77 \times k$, $-2015.22 \times k$, $-1315.78 \times k$, and $-790.22 \times k$, respectively. As the chain length increases, the absolute value of ΔS_{cyc} becomes smaller, indicating that the difference in conformational entropy between the cyclic polymers and the linear polymers is reduced. Furthermore, since the value of ΔS_{cyc} is negative, T_{mL} is obviously lower than T_{mC} , which is consistent with the observations in Fig. 4. Based on our discussions above, Fig. 5 fur-

ther demonstrates the fitting of Eq. (12) with our simulation results of the filled systems and the unfilled systems, in which $T_{\text{mL}}/T_{\text{mC}}$ is taken as the ordinate and the chain length is taken as the abscissa. In the fitting process, we treat $\frac{T_{\text{mL}}^0 Qk}{\Delta h_f^0}$ as one

independent fitting parameter B , and speculate that the corresponding value should be positive. It can be seen from Fig. 5 that the fitted curves of the filled polymer systems and the unfilled polymer systems are almost coincident. As we described in Fig. 4, the presence of nanofiller leads to an increase in T_{m} of both the cyclic polymers and the linear polymers. Since the ordinate is $T_{\text{mL}}/T_{\text{mC}}$, the effect of nanofiller is offset, resulting in the consistent fitting curves for the filled systems and the unfilled systems. According to our simulation results, the values of fitting parameter B for the filled systems and the unfilled systems after fitting are 0.1699 and 0.19618, respectively, which are positive and approximate as we expect. In addition, the R squared values of the fitting for the filled systems and the unfilled systems are 0.99509 and 0.99794, respectively, indicating that Eq. (12) fits well with our simulation results. These results further reflect the rationality and reliability of Eq. (12).

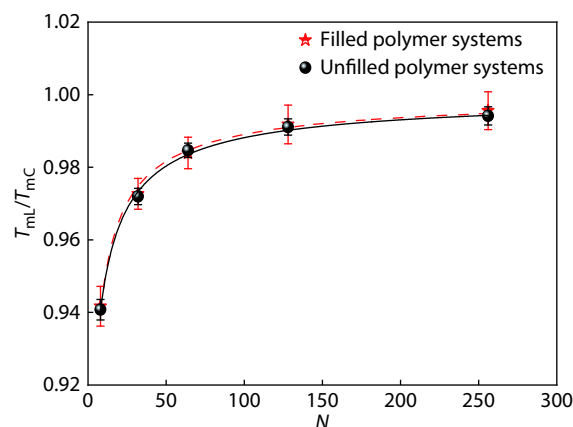


Fig. 5 Fitting of the relationship between the melting points of the filled/unfilled cyclic polymers and that of their linear analogs with different chain lengths based on Eq. (12). The dots denote the simulation results, and the solid line denotes the fit curve.

Subsequently, we perform isothermal crystallization at several temperatures close to T_c of the corresponding systems, and find that $T = 2.6$ is a suitable temperature to observe the crystallization process for most systems. However, considering the lower T_c of the systems with shorter linear chains, crystallinity variations of isothermal crystallization at $T = 2.4$ are also shown in Fig. 6. In our previous simulations, the effect of nanofiller on isothermal crystallization of different polymers has been investigated, and the simulation results show that the addition of nanofiller can accelerate crystallization and increase the final crystallinity.^[29–32] Therefore, we speculate that the nanofiller can have similar effect in the current simulation. Here, due to the difference in the optimum crystallization temperature between the filled systems and the unfilled systems, the isothermal crystallization process is not supplemented with the unfilled systems for comparison.

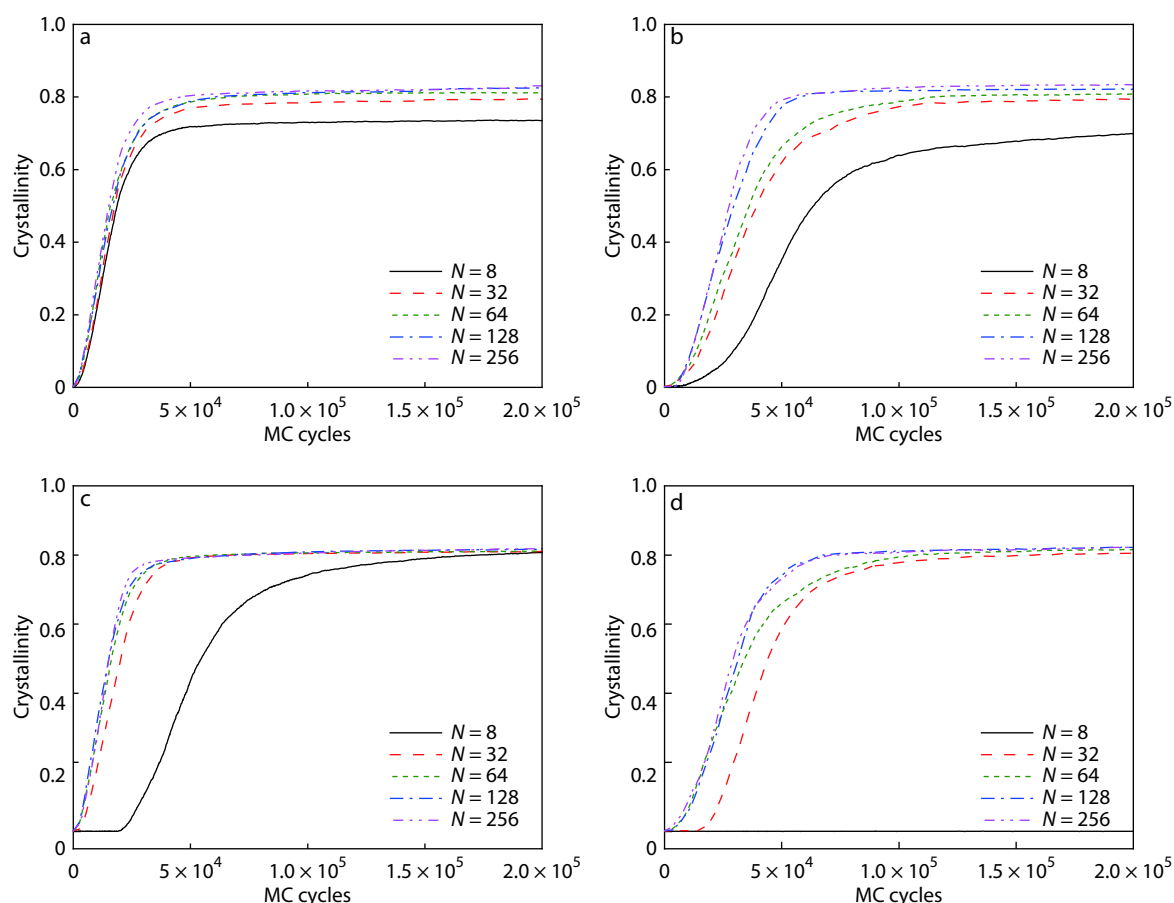


Fig. 6 Crystallinity evolutions for the filled cyclic polymer systems with different chain lengths under (a) $T = 2.4$ and (b) $T = 2.6$; Crystallinity evolutions for the filled linear polymer systems with different chain lengths under (c) $T = 2.4$ and (d) $T = 2.6$.

As illustrated in Fig. 6, the crystallinity curves for the filled cyclic polymer systems and their linear analogs both increase with increasing simulation time, indicating the occurrence of crystallization. Furthermore, it seems that different filled systems exhibit different crystallization rates. Thus, we further study the relationship between crystallization rates and chain length in the filled cyclic polymer systems and their linear analog. In the current simulation, we regard the semi-crystallization time as the simulation time required to complete half of the final crystallization. Then, the crystallization rate can be estimated according to the slope of the crystallinity curve at semi-crystallization time. Fig. 7 displays the evolution of the crystallization rates as a function of chain length for the filled cyclic polymers and analogous linear polymers under different temperatures. Obviously, the decrease in temperature can accelerate crystallization. In addition, as the chain length increases, the crystallization rate initially grows up rapidly and then continues to increase at an extremely low rate. Overall, the crystallization rate increases gradually with increasing chain length. In general, the crystallization rate under isothermal conditions is codetermined by nucleation and growth kinetics. Previously, a bell-shaped curve for the overall crystallization rate of PCL within a wide range of molecular weights has been reported, and this behavior has been attributed to the competition between two different factors: diffu-

sion which reduces growth kinetics at high molecular weights and supercooling which increases the crystallization driving force at low molecular weights.^[10,52] However, the effect of diffusion controlled by entanglement on growth kinetics in our current solution systems is negligible, which leads to differences between our simulation results and those reported in the literature at high molecular weights.^[52] Moreover, the cyclic polymers exhibit higher crystallization rate than the linear polymers of same chain lengths at identical crystallization temperatures, especially for the systems with shorter polymer chains. This phenomenon can be explained by the thermodynamic factor controlled by supercooling. When molecular chains are relatively short, the degree of supercooling of the cyclic polymers is much larger than that of the linear polymers, thus leading to higher crystallization rate. When molecular chains are relatively long, the difference in the crystallization rate between cyclic polymers and linear polymers becomes smaller at identical temperatures due to the slight difference in the degree of supercooling. It has also been reported in experiments that the difference in crystallization rate between cyclic and linear PCL gradually becomes smaller at higher molecular weights.^[2]

Since $\langle R_g^2 \rangle$ is a typical parameter used to describe conformational characteristics of polymer chains, we further monitor the evolution curves of $\langle R_g^2 \rangle$ during isothermal crys-

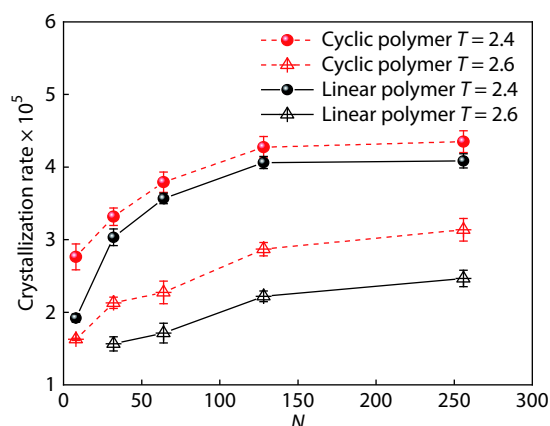


Fig. 7 Crystallization rates as a function of chain length for the filled cyclic polymers and analogous linear polymers.

tallization for these corresponding systems, as displayed in Fig. 8. It can be seen that with increasing simulation time, the values of $\langle R_g^2 \rangle$ decrease first and then gradually stabilize, corresponding to the occurrence of crystallization process. This trend is also present in the systems with shorter polymer chains, even if it is not obvious. Additionally, the values of $\langle R_g^2 \rangle$ increase significantly with increasing chain length, which can be explained by the classical theory of conformational statistics.^[53] Furthermore, the equilibrium state obtained after the relaxation process can be treated as the initial state for subsequent crystallization. Thus, Fig. 8(c) further illustrates the evolution curves of $\langle R_g^2 \rangle$ for the filled cyclic and linear polymers with different chain lengths under the equilibrium state. Compared with $\langle R_g^2 \rangle$ of the cyclic polymers under the equilibrium state, the analogous linear polymers display larger values of $\langle R_g^2 \rangle$. This phenomenon indicates that the cyclic polymers exhibit more compact conformations and smaller conformational entropy caused by the absence of chain ends, which is consistent with our descriptions above.

Fig. 9 demonstrates the final crystalline morphology of the cyclic polymers with different chain lengths and that of the corresponding linear polymers. It should be noted that current simulations are carried out in a cubic lattice box with periodic boundary conditions. Namely, when one molecular chain leaves the cubic lattice box from any boundary position, it will enter the cubic lattice box from another relative boundary position again. In this way, the finite size effect of simulation box can be avoided. Thus, the cubic lattice box does not limit the growth of the crystal or adversely affect the analysis of the results. Obviously, typical NHSK structure, in which the central one-dimensional nanofiller acts as shish and surrounding lamellar crystals orienting along the long axis of the nanofiller serve as kebabs, can be observed in all the systems. Such structure has also been found in linear polymer solutions filled with one-dimensional nanofillers.^[23–25] This result implies that the effect of chain topology on the final crystalline morphology in the filled polymer systems is not significant, which has also been observed in the unfilled polymer systems.^[2] Since the crystalline morphologies of the cyclic polymers and the linear polymers are identical, we can speculate that the formation mechanism of

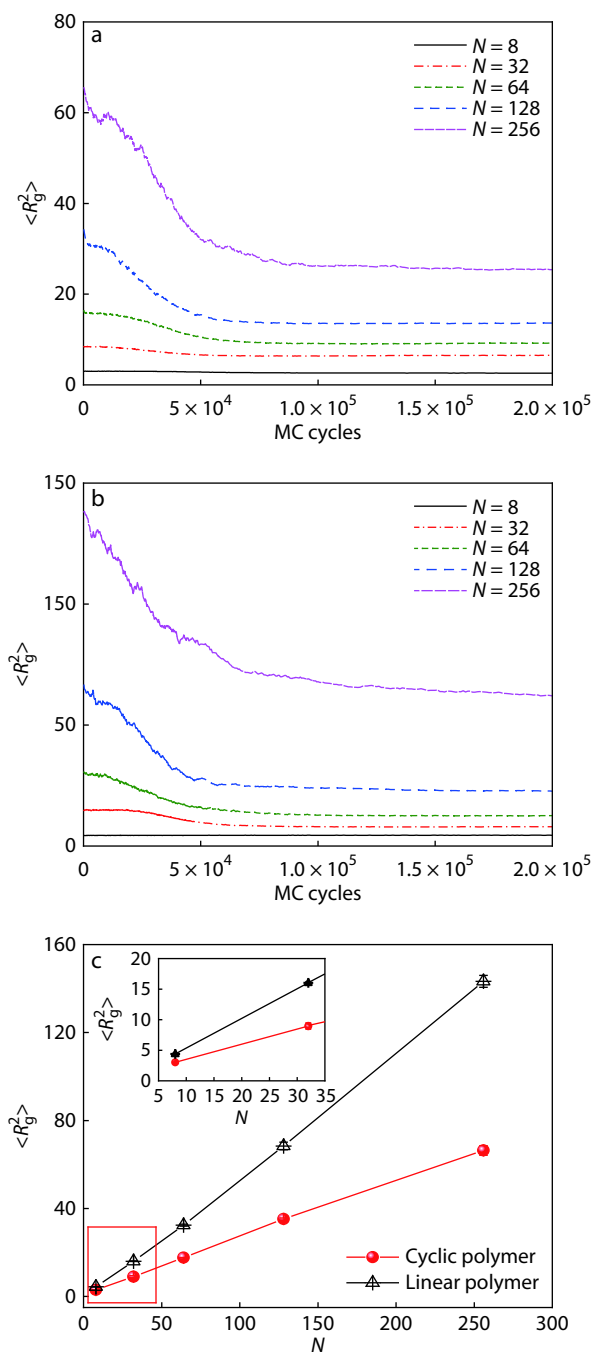


Fig. 8 (a) Evolution curves of $\langle R_g^2 \rangle$ for the filled cyclic polymers with different chain lengths during isothermal crystallization; (b) Evolution curves of $\langle R_g^2 \rangle$ for the filled linear polymers with different chain lengths during isothermal crystallization; (c) Evolution curves of $\langle R_g^2 \rangle$ for the filled cyclic and linear polymers with different chain lengths under the equilibrium state. For a clearer comparison, the inset is the partial enlargement of evolution curves of $\langle R_g^2 \rangle$ for the systems with shorter polymer chains.

the NHSK structure in the linear polymers is also applicable to the NHSK structure in the cyclic polymers. For linear polymer systems, the detailed formation process of the NHSK structure has been revealed in both experiments and simulations.^[23,24,30] Generally, at the early stage of crystalliza-

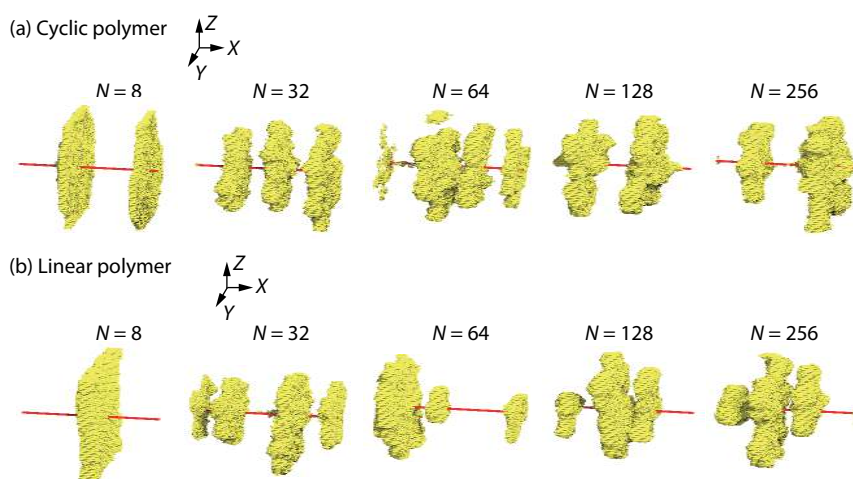


Fig. 9 (a) Snapshots of final crystalline morphologies for the filled cyclic polymers with different chain lengths at the later stage of crystallization; (b) Snapshots of final crystalline morphologies for the filled linear polymers with different chain lengths at the later stage of crystallization. Here, the yellow cylinders and the red strip stand for the crystalline bonds and the one-dimensional nanofiller, respectively.

tion, under the attractive polymer-filler interactions, chain segments are adsorbed on filler surface and adjust conformation to orient along the long axis of the filler. Subsequently, these oriented chain segments participate in heterogeneous nucleation and eventually grow into lamellar crystals. Previously, based on MC simulations, we also detected the formation process of the NHSK structure in different linear polymer systems filled with one-dimensional nanofiller.^[29–32] To more accurately describe the crystalline morphology, the lamellar thickness of the NHSK structure shown in Fig. 9 is further calculated. In the current simulation, the average length of the crystal stems in each lamellar crystal is considered as its thickness. Then, the thickness of each lamellar crystal in the NHSK structure can be calculated separately, and the average value is taken as the lamellar thickness of the NHSK structure formed in the corresponding systems. As illustrated in Fig. 10, the average lamellar thickness of the NHSK structure increases gradually with increasing chain length. It is worth not-

ing that the average lamellar thickness of the NHSK structure formed in the cyclic polymers is higher than that formed in the analogous linear polymers, although their extended-chain length is only about one half of their linear analogs. Shin *et al.* reported similar results for linear and cyclic PLLA, and they attributed this phenomenon to the lack of multiple chain folding in cyclic polymer chains due to the topological constraints on lamellar folding.^[2,14] Similar phenomena have also been found experimentally by Su *et al.* in the case of PCL crystals.^[3]

CONCLUSIONS

In the present work, the effects of chain topology and chain length on crystallization of polymer nanocomposites are revealed by dynamic MC simulations. We find that as the chain length increases, the melting temperature, the crystallization temperature, and the crystallization rate of the corresponding systems show a tendency to increase first and then gradually stabilize, which can be attributed to the lower degree of supercooling and higher nucleation barrier for shorter chains. Furthermore, compared with the filled linear polymers, the higher melting points and faster crystallization can be observed in the analogous cyclic polymers, especially for the systems with shorter polymer chains. Such phenomenon is caused by the fact that the chain ends of the linear polymers can act as lattice defects to lower the melting point, resulting in a decrease in the degree of supercooling and crystallization rate. Thus, the cyclic polymers exhibit higher melting points and crystallization rates due to the lack of chain ends and more compact conformation. Based on the Thomson-Gibbs equation, the relationship between the melting point of the cyclic polymers and that of their linear analogs under different chain lengths is further theoretically analyzed, which is consistent with our findings. In addition, the presence of nanofiller leads to the formation of NHSK structure in all the systems, while the thickness of kebabs formed by the cyclic chains is greater than that formed by the linear chains.

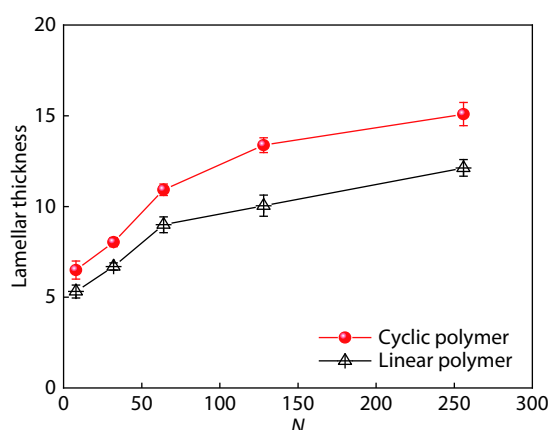


Fig. 10 Variations of lamellar thickness of the NHSK structure formed in different systems, *i.e.*, filled cyclic and linear polymers with different chain lengths.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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