

# Effect of Crystallization and Entropy Contribution Upon the Mechanical Response of Polymer Nano-fibers: A Steered Molecular Dynamics Study

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## Electronic Supplementary Information

**Abstract** The mechanical response of polyethylene nano-fibers with the same chain length but different chain numbers are studied by using steered molecular dynamics simulations. The shrinking or stretching forces acted on the chain ends are investigated according to the chain-end distance and temperature under isothermal or continuous warming-cooling conditions, respectively. An inflection point is found in the Force-Distance response when temperature is below 500 K. This inflection point is related to the balance between entropy force and inter-monomer interaction and it reflects the strong effect of crystallization on the mechanical response of the nano-fibers. The force at inflection point is also affected by the buckling effect due to increased stiffness when crystallization occurs. The two stages found in the Force-Temperature response and the difference between the shrinking and stretching forces indicate the hysteresis of crystallization and melting. The forces at different shrinking and stretching rates reveal the entropy contribution upon the mechanical response, indicated by the Ramachandran plot of dihedrals. The chain-conformation entropy is majorly contributed by dihedrals and is quantified by the information entropy of dihedrals, which has a highly similarity to the mechanical Force-Temperature response. The enlarged forces in multiple chains over a single chain are attributed to the enhanced dihedral-conformation entropy. Our study provides a new insight to the dynamically mechanical response of polymer nano-fibers according to the effect of crystallization and entropy contribution.

**Keywords** Polymer fibers; Crystallization; Entropy contribution; Mechanical response

**Citation:** Ma, R.; Xu, D.; Luo, C. F. Effect of crystallization and entropy contribution upon the mechanical response of polymer nano-fibers: a steered molecular dynamics study. *Chinese J. Polym. Sci.* 2023, 41, 465–474.

## INTRODUCTION

Polyethylene is one of the top five general-purpose plastics in the world, and its properties are mainly affected by the crystalline morphology. Ultra-high molecular weight polyethylene (UHMWPE) fiber is one of the highest specific strength and modulus fibers in the world today. However, due to the limitations of experimental observations and classical theoretical models, the research on the crystallization of polyethylene is not yet mature, especially the lack of molecular-scale analysis of the mechanical response.

Since Staudinger established the concept of polymer or macromolecule in the 1920s, it has been the most commonly used term in the extensive academic research and industrial development of synthetic polymers.<sup>[1]</sup> Polymers are a group

of chain-like macromolecules composed of many repeating units such as polyethylene (PE) and polypropylene (PP). Because of its good cost-performance, excellent processing performance and mechanical properties, polymeric material is widely used in daily life, industry, agriculture, health care, military, aerospace and other fields.<sup>[2]</sup> Semi-crystalline polymers are the major materials used in current industry. The properties of semi-crystalline polymers are mainly determined by the crystalline structure, which is influenced by the polymer structure and the crystallization process. It is very important to investigate the crystallization process of polymers. For polymer fibers, such as UHMWPE, it is needed to study the chain structure of polymers, not only for the purpose of mechanistically understanding the structural properties of polymers but also for the development of high-performance polymer materials.<sup>[3]</sup>

Polyethylene is the most widely used semi-crystalline polymer material. Many experiments have been conducted on polyethylene materials from different viewpoints, but they

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Received May 4, 2022; Accepted June 2, 2022; Published online September 21, 2022

are mostly limited to the macroscopic range. The knowledge of the factors affecting the properties of polyethylene at molecular level is still lacked, especially of the mechanical properties. With the rapid development of computer hardware and software technology, computer simulations have become an important research tool to study the crystallization process and mechanism of polymers on a molecular scale. Since the 1950s, researchers have used computer simulations to study the properties of polymers. In 1988, Roe *et al.*<sup>[4]</sup> applied computer simulations to the study of the crystallization process of short-chain alkanes. In 1993, Kavassalis *et al.*<sup>[5]</sup> observed the process changing from random wire clusters to crystalline structures in PE. Liao *et al.*<sup>[6]</sup> investigated the crystallization process of polyethylene single chains with different chain lengths at 300 K. It was found that the polyethylene chains change from random nematic clusters to neatly aligned polyethylene chain structures as the simulation proceeds. Fujiwara *et al.*<sup>[7]</sup> studied polyethylene single chains with chain length of 500 and found that polyethylene single chains would first form a random nematic structure at 800 K, and the randomly arranged polyethylene chains would gradually become ordered as the temperature decreases. That is, crystallization would occur, and the lower the temperature, the higher the crystallinity would be. Koyama *et al.*<sup>[8,9]</sup> investigated the degree of localized ordering of polyethylene single chains using a united-atom model by lowering the temperature from 600 K to 120 K. The study showed that the degree of ordering gradually increased with decreasing temperature and the crystallization took place in the form of folding of polyethylene chains. Waheed *et al.*<sup>[10]</sup> developed a model by which it is possible to establish the crystallization rate as a function of temperature and molecular weight of polyethylene chains. Yu *et al.*<sup>[11]</sup> studied the changes of crystallinity and entanglement of single-chain polyethylene during the crystallization process, and the crystallinity is increased and the entanglement decreased as the crystallization process proceeded. Kavassalis *et al.*<sup>[5]</sup> studied the effect of chain length on the crystallization process of polyethylene chains and found that the crystallization process of polyethylene chains does not undergo local collapse and forms random wire clusters directly when the chain length is below 1200 C atoms. Hossain *et al.*<sup>[8]</sup> investigated the effects of temperature and rate on the mechanical properties, energy changes, and entanglement of polyethylene during stretching of amorphous polyethylene samples using a union-atom model. Balijepalli *et al.*<sup>[12]</sup> conducted a statistical study of the conformation of amorphous regions in semicrystalline polyethylene. The results show that the number of bridge-like structures varies with the chain length in the NVT simulation. Hong *et al.*<sup>[13,14]</sup> investigated the changes in mechanical properties of a semicrystalline polyethylene model when subjected to three stresses: compression, tension, and shear. The results show that when subjected to tensile action, wafer slippage occurs in the elastic phase and the Young's modulus increases gradually with increasing crystallinity.<sup>[15,16]</sup> Queyroy *et al.*<sup>[17]</sup> studied the tensile process of semicrystalline polyethylene and the results showed that the yield limit is sensitive to the thickness of the crystalline zone. Yeh *et al.*<sup>[18]</sup> investigated the effect of system size on the process during

stretching using a united-atom model of semicrystalline polyethylene, and the study showed that system size has little effect on the stretching process. Li *et al.*<sup>[19,20]</sup> used the Monte Carlo method to stretch semicrystalline polyethylene and carefully analyzed the elastic deformation, yield limit, and Poisson's ratio.

The fundamental physics of polymers not only provides an understanding of polymer processing and product properties, but also provides a physicochemical background to more complex behavior of biological macromolecules, including DNA, RNA and many proteins.<sup>[21–23]</sup> Today, more than two-thirds of the world's commercial polymers are semi-crystalline. The semi-crystalline texture is composed of alternating amorphous and crystalline layers with characteristic thicknesses, which determine the thermal and mechanical properties of the polymer.<sup>[24–26]</sup> Therefore, the study of polymer crystallization behavior is very important. In previous simulation researches, spontaneous chain folding during polymer crystallization has been commonly observed.<sup>[27,28]</sup> It also confirmed the crystallization behavior of polyethylene.<sup>[29,30]</sup> In the process of polymer crystallization, the molecular-scale kinetic details cannot be obtained in experiments, but it can be easily obtained in computer simulations.<sup>[31]</sup> Although computer simulation cannot completely replace experiments, it can be used to guide experiments and verify certain theoretical hypotheses, thus promoting the development of theories and experiments.<sup>[32]</sup> This advantage makes computer simulation valuable in scientific researches.<sup>[33,34]</sup> In 1985, for semiconductors and metals, which are difficult to model because of the potential function, Car *et al.*<sup>[35]</sup> proposed a first-principles molecular dynamics method that organically unifies the electron theory and the molecular dynamics method. In 1991, Cagin *et al.*<sup>[36]</sup> further proposed a grand canonical ensemble molecular dynamics method applied to deal with adsorption problems. In molecular dynamics simulations, the role of force fields is crucial. The OPLS force field and the OPLS-AA force field used in this study were developed by Jorgensen *et al.*<sup>[37,38]</sup> This force field has a wide range of applications and can be applied to molecular dynamics simulations of polymers.<sup>[39]</sup>

Over the past decades, many researchers have investigated the crystallization process of PE chains using molecular simulations, but the crystallization behavior of PE is still not yet well established due to the limitations of experimental tools and classical theoretical models. In this paper, we construct a series of simulations to study the polymer fibers consisting of several PE chains. We use steered molecular dynamics simulations to explore the mechanical behavior of the polymer nano-fiber during crystallization process at the molecular scale. We will focus on the effect of crystallization and entropy contribution to the dynamical response of the polyethylene nano-fibers.

## MODELS AND METHODS

The steered molecular dynamics (SMD)<sup>[40]</sup> simulations in this work are performed by the Gromacs-2019.5 software package<sup>[41]</sup> using the all-atom model in OPLS force field (OPLS-AA). The interactions between atoms consist of bonded (bond, angle, and dihedral) and non-bonded (van der Waals and

Coulomb) potentials. The non-bonded interactions are cut off at 0.95 nm and a non-periodic boundary condition is used. The simulation temperature is controlled by the V-rescale thermostat method, which is an optimized thermostat with random effect to the simple velocity rescaling. The leap-frog integration algorithm is used with an integration step of 2 fs. More details of the OPLS-AA force field are presented in the electronic supplementary information (ESI).

We consider a bundle of PE chains as a polymer nano-fiber to study the effect of crystallization upon the mechanical response. We design four situations of nano-fibers with different chain numbers ( $N_{\text{chain}}$ ): 1, 4, 9 and 16-PE chains with identical initial end-to-end distance of 25 nm as shown in Fig. 1, respectively. In the following discussion, we simply note the end-to-end or chain-end distance as  $L$  for convenience. Each PE chain consists of 200 carbons and 402 hydrogens ( $\text{C}_{200}\text{H}_{402}$ ). The forces of stretch or shrink are applied on the two ends (carbons) of all chains along the  $x$  direction, as shown in Fig. 1(a). The disordered arrangement of chain ends on one side of each PE chain in cross-sectional view is shown in Fig. 1(b). We control the chain ends getting closer or farther away from each other along  $x$ -axis during the shrinking or stretching of SMD simulations, at different rates and temperatures. The initial molecular chain spacing is set as 0.3 nm. We note that the chain spacing distance and the arrangement pattern of chain ends only affect the local structures near the chain ends and almost have no effect on the force response.

We analyze the sum of the forces on the chain ends for all chains ( $F$ ), the total force divided by chain numbers ( $F^* = F/N_{\text{chain}}$ ) and the total force divided by chain numbers and the temperature ( $F^{**} = F/N_{\text{chain}}T$ ) in the simulations, *i.e.*, we

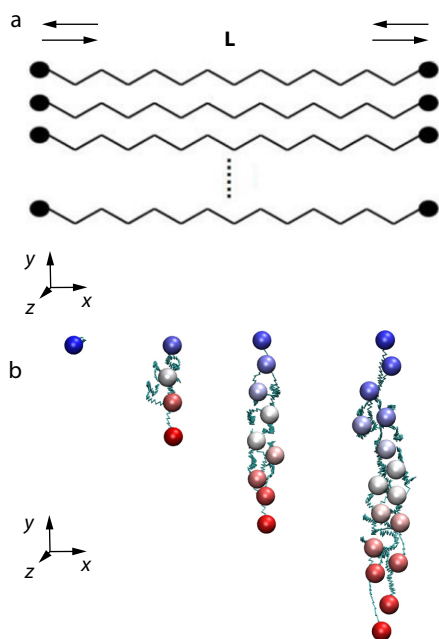


**Fig. 1** (a) Sketch of PE chains with the same chain-end distance ( $L=25$  nm) in the initial state. The black dots represent chain ends on which forces are applied, the zig-zag lines represent PE chains, and the arrows represent the direction of shrinking or stretching. (b) Cross-sectional view of the chain ends on one side (1, 4, 9 and 16 chains, respectively).

denote the chain-normalized force and the chain-temperature-normalized force as  $F^*$  and  $F^{**}$ , respectively. The analysis of the shrinking and stretching behavior of PE chains at different rates and temperatures allows us to investigate the effect of crystallization and entropy contribution to the mechanical response of polymer nano-fibers.

## RESULTS AND DISCUSSION

### Isothermal Shrinking and Stretching

In the isothermal simulations, we first shrink and stretch the PE chains for 20 recycles as a relaxation process, then calculate the forces on the chain ends in the subsequent cycles. In each cycle, the chain-end distance of a nano-fiber ranges from 5 nm to 25 nm during the shrinking and stretching process. The simulation temperatures range from 200 K to 1000 K.

To give a general mechanic response picture of the nano-fiber, we plot the forces during shrinking and stretching for 10 times as a function of chain-end distance in Fig. 2. Here, the simulation temperature is 500 K and the shrinking or stretch rate is 0.001 nm/ps. At this temperature, we can see that there is no significant difference in the Force-Distance curves between the shrinking (red lines) and stretching (blue lines) process. For both systems of 4 and 9-PE chains, the Force-Distance curves exhibit the same trend and there is an inflection point roughly at 18 nm. The force keeps almost un-

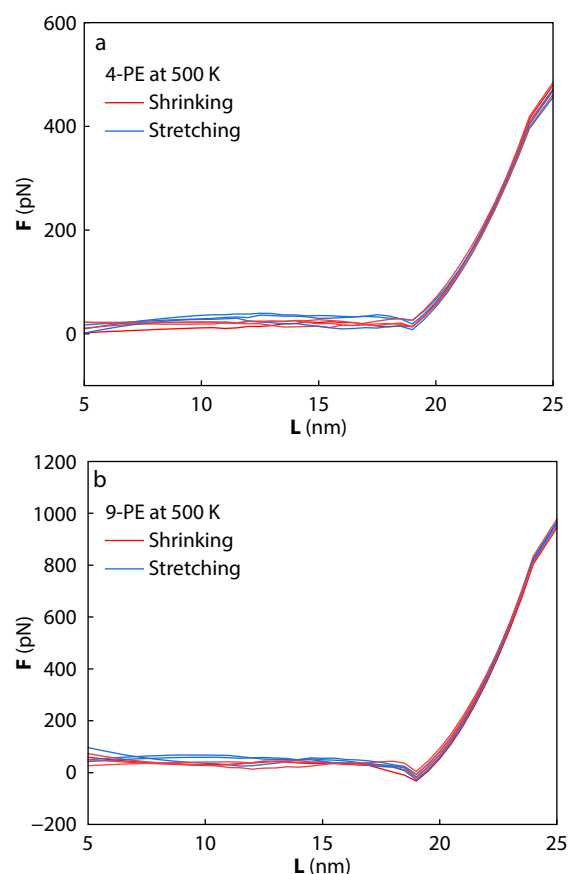


**Fig. 2** Forces on chain ends ( $F$ ) during shrinking and stretching for 10 cycles as a function of chain-end distance for (a) 4-PE chains and (b) 9-PE chains at 500 K. The shrinking or stretch rate is 0.001 nm/ps.

changed around zero when the chain-end distance is below 18 nm, and it increases significantly when the chain-end distance is above 18 nm. We attribute this inflection point at 18 nm as the happening of chain collapsing, where the entropy force and the intra-chain attraction force are balanced. For the OPLS-AA force field, highly oriented PE chains can start to crystallize at the temperature of 500 K, although the crystallinity at 500 K is low. All chains are stretched by the strong force to roughly straight conformations when the chain-end distance is larger than 18 nm. However, chains can form chain folds due to crystallization when the chain-end distance is less than 18 nm and at low temperature.

The mechanical response (Force-Distance curve) of fast increasing force according chain-end distance at large stretched case can be explained by the model of worm-like chain. From a simplified theoretical view of this force, it originates from the change of entropy in chain conformation, which is roughly proportional to the chain-end distance. The small force around zero for the chain-end distance is less than 18 nm indicates the force is origins from the interactions between atoms, which is independent to the chain conformation and the chain-end distance. As chains folds are formed at this situation, the force is therefore related to the lateral tearing force.

We notice that the force has a notable drop at the inflection point of  $L=18$  nm. We attribute this drop of force to the buckling effect, which is strongly related to the increase of chain stiffness and crystallization when temperature is low. The bucking effect is stronger when the chain is stiffer or the independent chains form a stiff bundle in the case of crystallization. We will discuss this topic further in the later sections. Here, we note that the inflection point at  $L=24$  nm is not a real inflection point but a systematic error near the edge of the largest expected pull range, by using the virtual springs in

SMD as detailed in ESI.

To give a visual impression of the simulation system, we show the snapshots during simulations for the four systems (1, 4, 9 and 16-PE chains) at different temperatures in Fig. 3. Here, the chain-end distance is 5 nm ( $L=5$  nm). We can see that at lower temperatures (300 and 400 K), all systems can crystallize, although the stem length in crystalline structure of 1-PE chain is shorter than the others. The inter-chain orientation of multi-chain systems significantly increase the stiffness of the nano-fibers. At higher temperatures (500 K, 600 K), the snapshots indicate all nano-fibers do not form a crystalline structure and the PE chains are randomly arranged like in the molten state. However, some kind of crystallization happens for multi-chain systems at 500 K indicated by using order parameters such as  $Q_6$  or average stem length.

We systemically studied the shrinking and stretching behavior of the PE nano-fibers with the initial chain-end distance of 25 nm at a rate ranging from 0.01 nm/ps to 0.001 nm/ps and at different temperatures from 200 K to 1000 K. When a lower rate of 0.001 nm/ps is applied, the Force-Distance curve during shrinking and stretching is smoother than the situation when the rate is 0.01 nm/ps. The difference of force values between the rate of 0.01 and 0.001 nm/ps is small but notable, which we will discuss later. Here we first focus on the analysis of the mechanical response at a slow rate of 0.001 nm/ps.

The chain-normalized force curves ( $F^* = F/N_{\text{chain}}$ ) as a function of chain-end distance ( $L$ ) are shown in Fig. 4. We can see from each subplot that the force increases with temperature, which indicates that there is a strong entropy effect in the mechanical response of these nano-fibers. We will discuss the entropy effect separately in the later sections. Similar to Fig. 2, the inflection points of the Force-Distance curves at about 18 nm can be noticed at low temperatures, and it is more ob-

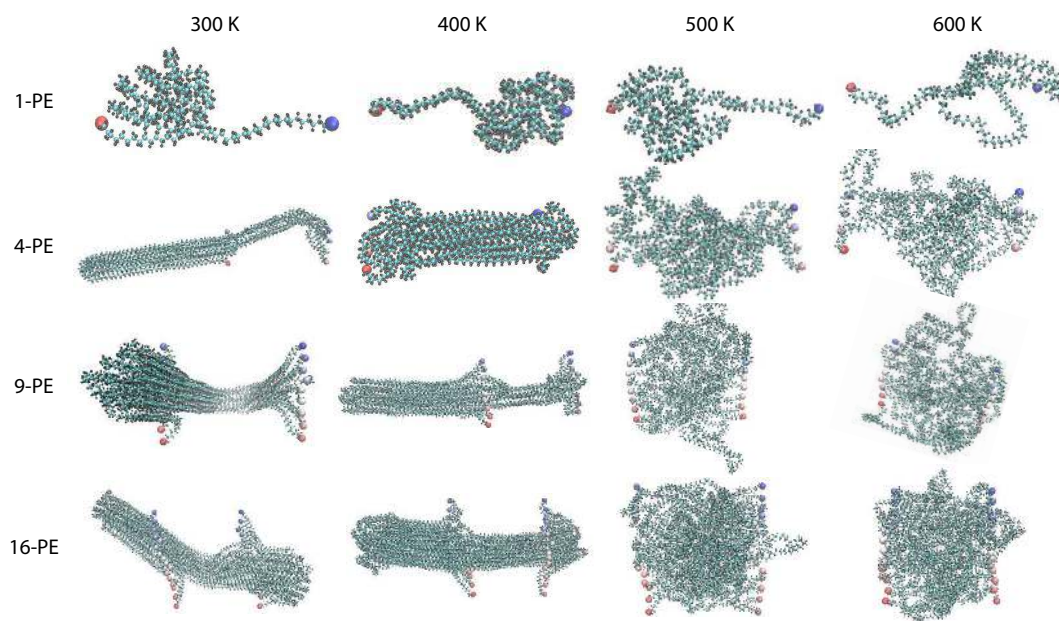


**Fig. 3** Snapshots during simulations for four systems (1, 4, 9 and 16-PE chains) with the chain-end distance of 5 nm at different temperatures (300K, 400K, 500K and 600K). We choose the moment after repeated 20 cycles of shrinking and stretching. The snapshots are generated by using the VMD software.<sup>[42]</sup>

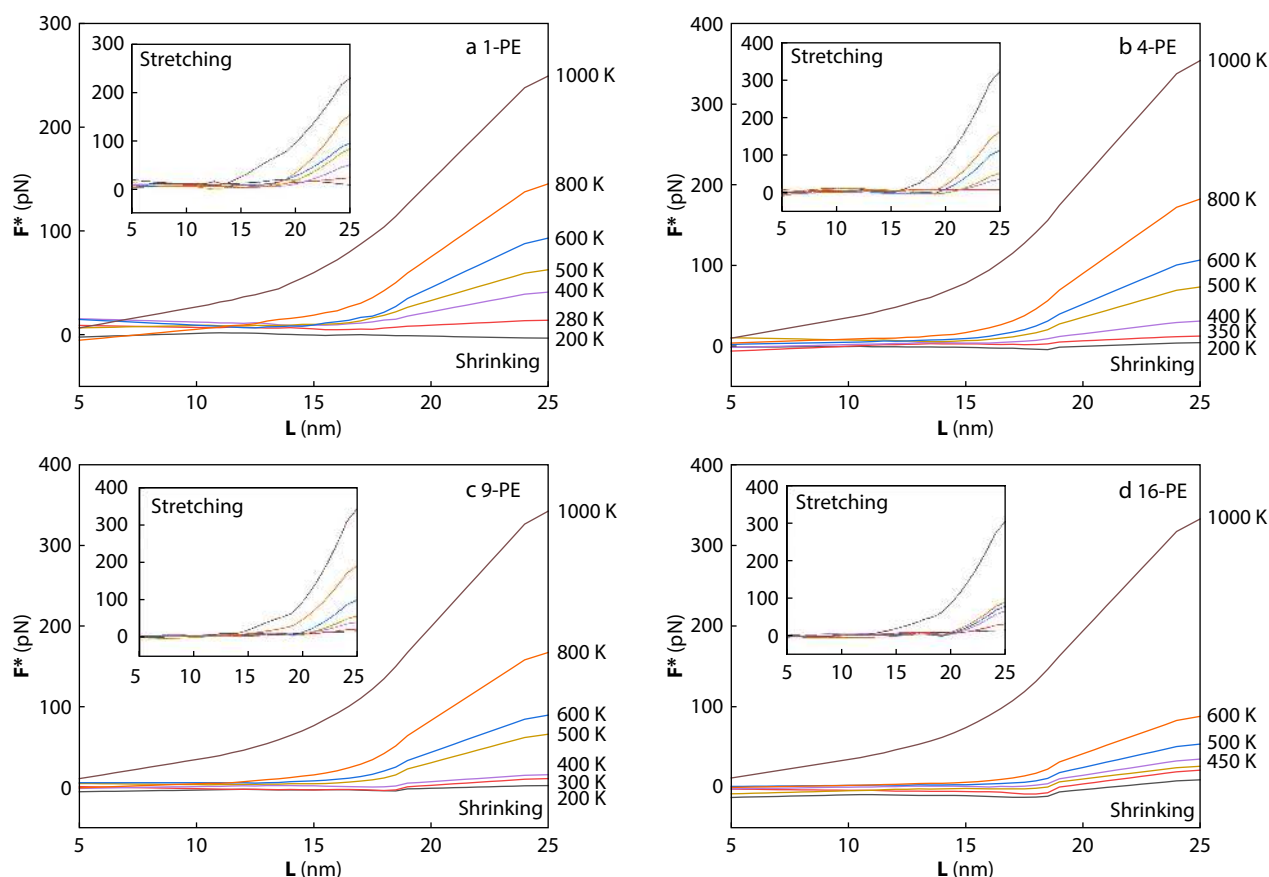


**Fig. 4** Chain-normalized force ( $F^*$ ) versus chain-end distance ( $L$ ) during shrinking and stretching for four systems: (a) 1-PE, (b) 4-PE, (c) 9-PE, (d) 16-PE. The shrinking or stretching rate is 0.001 nm/ps. Here,  $F^*$  denotes the force divided by the chain numbers as  $F^* = F/N_{\text{chain}}$ . Different colors in each subplot represent different temperatures. The simulation time for all these four subplots is 20 ns and the results are averaged from 10 cycles after 20 cycles of relaxation.

vious when there are more chains (9-PE and 16-PE), as shown in Figs. 4(c) and 4(d). As discussed above, the inflection point is related to the balance between the entropy force and the inter-monomer attraction force. Thus, if the temperature is higher, the balance length is shorter. When the chain-end distance is less than the inflection point, chains are collapsed or even are folded and crystallized. The force drop at the inflection point is related to the buckling effect, as mentioned above. We can see that the force drop is more obvious for thicker nano-fibers (9-PE and 16-PE chains) or at lower temperatures, as shown in Fig. 4. As the stiffness of chain bundles is highly related to the crystallization, this buckling effect is the evidence of effect of crystallization upon the mechanical response of nano-fibers.

### Continuous Warming and Cooling at Fixed Chain-End Distance

To verify the relationship between the chain-end distance and the temperature when the PE nano-fibers are shrunken and stretched, we fix the chain-end distance at four different values (5, 10, 15 and 25 nm). We heat and cool the chains with the temperature ranges from 200 K to 1000 K for 100 ns. A clear tendency can be concluded from all subplots of Fig. 5 that the force increases with temperature, which corresponds to the conclusion from Fig. 4. We can find that there is only slight

difference of the forces between the warming and cooling process. It is notable that there is a transition at  $T=500$  K, above which the force is smooth and below which the force becomes fluctuated. This is again the evidence of effect of crystallization upon the mechanical response according to temperature.

We can see from each subplot in Fig. 5 that the greater the number of chains, the greater the change in force by temperature. We can also find that the change in force is larger when the chain end distance is larger. It indicates that as the chain-end distance increases, the restriction on the chain conformation increases, and the tension in the chains also increase during warming and cooling.

Since the temperature has a great influence on the force, and it is directly related to the entropy contribution, we normalize the force by dividing the number of chains and the temperature as  $F^{**} = F/N_{\text{chain}}T$ . We plot this chain-temperature-normalized force  $F^{**}$  versus temperature  $T$  in Fig. 6, where the chain-end distance  $L$  is fixed as 25 nm. From Fig. 6, we can see that the transition temperature is around 500 K in the shrinking diagram, but around 600 K in the stretching diagram. This is actually the hysteresis behavior of crystallization and melting. It supports our discussion above that the inflection point is related to the crystallization. The fluctuation of force below 500 K reflects the meta-states of crystalline structures, as the force is smooth when temperature is higher than

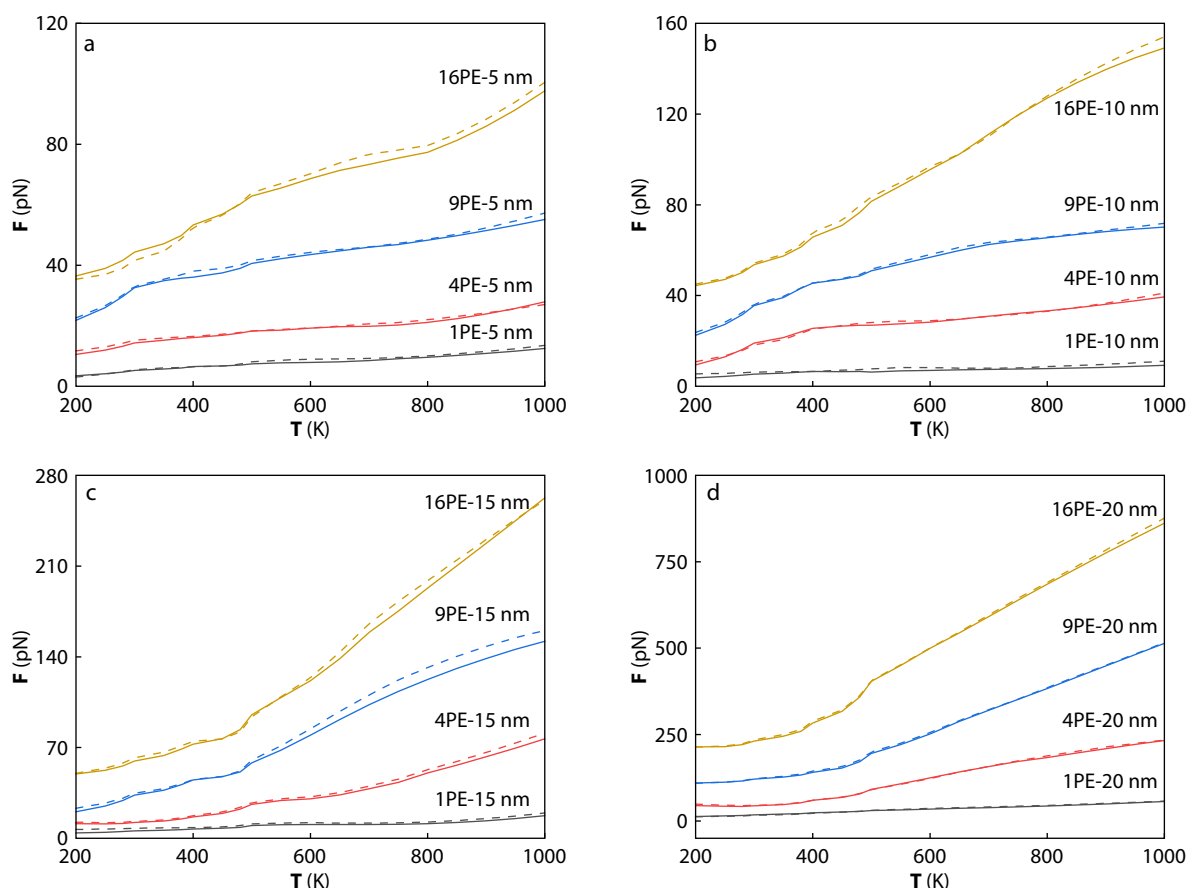


**Fig. 5** Force on chain ends ( $F$ ) as a function of temperature ( $T$ ) during continuous warming (solid line) and continuous cooling (dashed line) with fixed chains-end distance: (a) 5 nm, (b) 10 nm, (c) 15 nm, (d) 20 nm. The continuous cooling or heating time is 100 ns from 200 K to 1000 K.

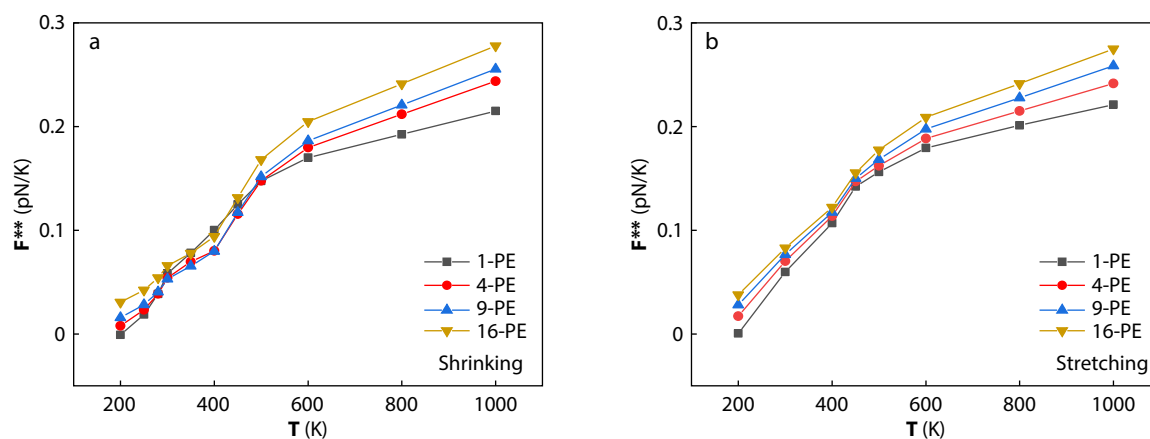


**Fig. 6** Chain-temperature-normalized force ( $F^{**} = F/N_{\text{chain}}T$ ) at the chain-end distance  $L=25$  nm as a function of temperature ( $T$ ) for (a) shrinking and (b) stretching. The shrinking or stretch rate is 0.001 nm/ps and the simulation duration is 20 ns.

600 K.

It is interesting to note that the value of chain-temperature-normalized force  $F^{**}$  increases as the number of chains and also temperature, as it is already divided by the number of chains  $N_{\text{chain}}$  and temperature  $T$ . This behavior happens in both shrinking and stretching process. It means the mechanical response of a multi-chain nano-fiber is not just an accumulation of the forces required to stretch each chain. It indic-

ates that the interactions between chains contribute to the total mechanical response in multi-chain nano-fibers, although the interactions are in the form of lateral forces. We notice that the difference of chain-temperature-normalized force between difference multiple chains is larger when the temperature is higher. This is a strong evidence that there is an entropy contribution to the mechanical response, which we will discuss in the following section.

In Fig. 6, the slopes of Force-Temperature curves at low temperature region are different in shrinking and stretching, indicating the deformation mechanisms are different. In our simulations, the shrinking could be related to crystallization while the stretching could be related to melting. According to the Ostwald's Rule, the crystallization involves many metastable states and the rate of structural change during shrinking is smaller than that during melting caused by stretching. In addition, the transition between latent heat and work can directly affect the force response. Further research about this is planned in the future.

### Entropy Contribution at Different Rates of Shrinking and Stretching

In addition to the evidence of entropy contribution to the mechanical response shown in Fig. 6, we also found that the difference of force at different shrinking and stretching rates is small but notable, which is related to the ergodic speed in the possible conformation space. As the all-atom model of OPLS-AA is used, the major contribution to the chain conformation is the possible states of dihedrals in four jointed carbons.

Ramachandran plot is also called  $[\phi, \psi]$  plot and applied widely in the structural analysis of proteins.<sup>[43]</sup> It represents the dihedrals of the  $\alpha$  carbons, taking the values of  $\phi$  and  $\psi$  as the abscissa and ordinate to specify a 2D figure. We draw the Ramachandran plots of dihedrals in the PE nano-fibers when the shrinking and stretch rate is 0.01 and 0.001 nm/ps at different temperatures in Figs. 7 and 8. Comparing with Fig. 7 and Fig. 8, we can find that the boundary of the spatial distribution map in Fig. 8 is clearer. As the temperature and the number of chains increase, we get a wider spatial distribution of the dihedral angles. It means that the arrangement of chains is more disordered and have larger entropy as the temperature and the number of chains increase, which is con-

sistent with our previous discussion of entropy contribution to the mechanical response.

To quantify this entropy of dihedral conformation, we introduce the concept of information entropy of dihedrals, which is originally proposed by Shannon in 1948.<sup>[44]</sup> Information entropy is a parameter used to measure the chaos degree of information in information theory. The more orderly a system, the lower the information entropy; conversely, the more chaotic a system, the higher the information entropy. Here, we use it to give a quantitative measurement of the conformation space of dihedrals. The calculation formula of the information entropy of dihedrals is  $S = -(\sum_{i=1}^n p_i \log p_i + \log N_g)$ . Where,  $p_i$  means the probability that a dihedral angle in the  $i^{\text{th}}$  grid by dividing the whole dihedral angle range into  $N_g$  isometric grids. For infinitely slow processes, the information entropy times the Boltzmann constant  $k_B$  is related to thermodynamic entropy of dihedrals, which is the major contribution of chain conformational entropy.

By summing the values of the probability of dihedrals in the Ramachandran plots, the information entropy of dihedrals can be obtained and shown in Fig. 9, according to the rate of 0.01 and 0.001 nm/ps. We note that the clearer images shown in Fig. 9 are due to more sampling points but the differences in information entropy are the results of different probability distributions not the number of sampling points. It can be seen that the information entropy of dihedrals  $S$  increases with the temperature and the number of chains. This means that when the temperature is higher and the chain numbers is larger, the dihedral conformation of the PE chains becomes more chaotic and entropy contribution is larger. We notice that the trend of  $S$  according to  $T$  is very similar to that of  $F^{**}$  according to  $T$  as shown in Fig. 6. This is a strong evi-

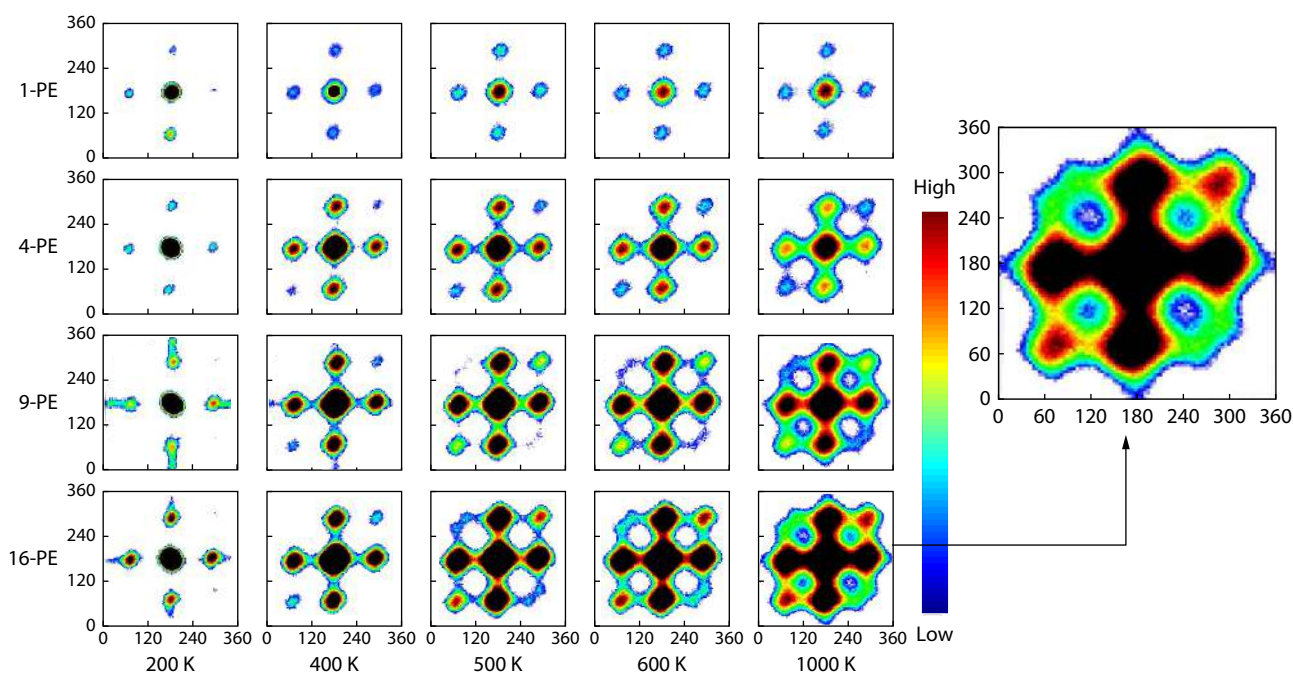


**Fig. 7** Ramachandran plots for four systems (1, 4, 9 and 16-PE chains) at different temperatures (200, 400, 500, 600 and 1000 K) when the shrinking and stretching rate is 0.01 nm/ps. The figures are plotted by using the Veusz software.

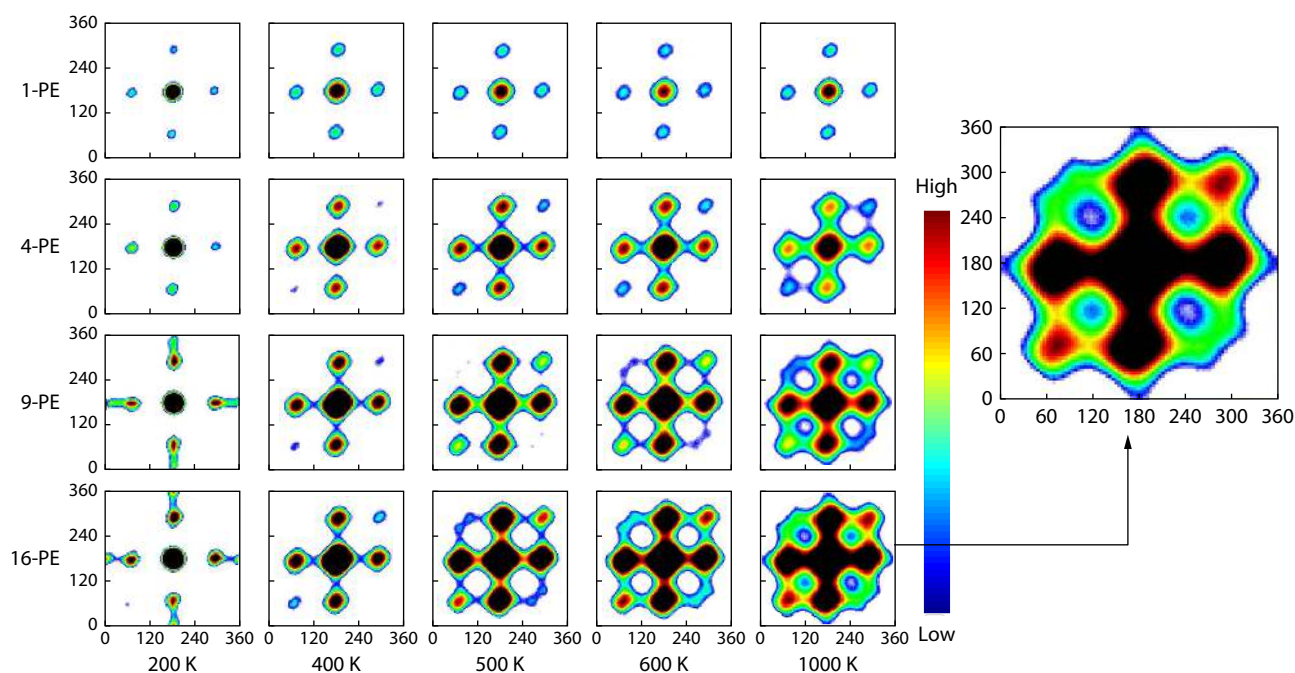


**Fig. 8** Ramachandran plots for four systems (1, 4, 9 and 16-PE chains) at different temperatures (200, 400, 500, 600 and 1000K) when the shrinking and stretching rate is 0.001 nm/ps. The figures are plotted by using the Veusz software.

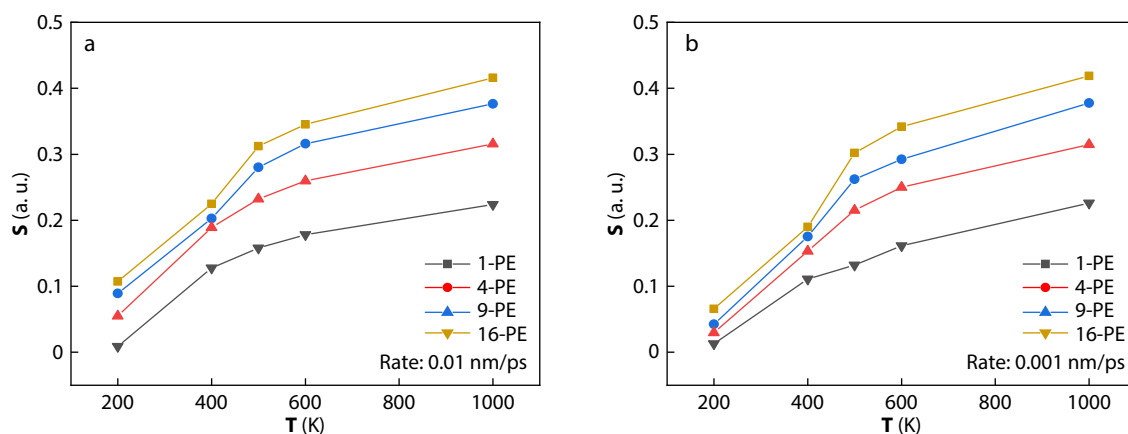


**Fig. 9** Information entropy of dihedrals ( $S$ ) as a function of temperature ( $T$ ) for the shrinking and stretching rate is (a) 0.01 nm/ps and (b) 0.001 nm/ps.

ence that the entropy contribution of dihedrals plays an important role in the mechanical response of PE nano-fibers.

## CONCLUSIONS

We focus on the influence of crystallization and entropy contribution upon the mechanical response of polymer nano-fibers by using steered MD simulations. Based on the simulation data and analyses presented in this work, we obtain the following conclusions.

1. The force acted on the chain ends increases with the chain-end distance, the temperature, and the number of chains. When the temperature is below the crystallization temperature, an inflection point in the Force-Distance curve is observed, which is related to the chain folding and buckling effect occurs at crystallization. The Force-Temperature re-

sponse also reflects strong effect of crystallization upon the mechanical response of the nano-fibers.

2. The entropy contribution upon the mechanical response is revealed by the Ramachandran plot and the information entropy of dihedrals. The difference of forces at different shrinking and stretching rates and the enlarged forces in multiple chains over a single chain are both the evidence of entropy contribution to the mechanical response of polymer nano-fibers.

Although our conclusions are based on polyethylene nano-fibers, we believe that the effect of crystallization and entropy contribution are important in the mechanical response of other polymeric fibers. Our study provides a new insight to understand the mechanism of and to improve the dynamically response of polymer nano-fibers. The results are also heuristic to understand the crystallization in polymer fibers.

## NOTES

The authors declare no competing financial interest.

### Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2817-y>.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 21873093 and 22103080). We gratefully acknowledge HZWTECH for providing computation facilities.

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