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Cite this article as:

Zhang Xiang, Wang Yu, Xia Ru, Wu Bin, Chen Peng, Qian Jia-Sheng, Liang Hao-Jun. Effect of Chain Configuration on Thermal Conductivity of Polyethylene—A Molecular Dynamic Simulation Study[J]. *Chinese J. Polym. Sci.*, In press. doi: 10.1007/s10118-020-2466-y

View online: <https://doi.org/10.1007/s10118-020-2466-y>

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Effect of Chain Configuration on Thermal Conductivity of Polyethylene—A Molecular Dynamic Simulation Study

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Abstract Stretched polyethylene (PE) fibers are found to have super high thermal conductivity, while the bulk of polyethylene is usually thermal insulating even for those with high crystalline degree. A molecular dynamic simulation is deliberately carried out to examine the relationship between chain configuration and thermal conductivity of polyethylene. In this simulation study, independent and interacting PE chains being stretched are compared with the aim to find out the effect of stretching on thermal conductivity of PE. Various crystallization conditions for PE bulk are considered. It is found that heat transports predominately along the covalent chain rather than across chains in PE crystals. Our simulation study helps to understand experimental findings on thermal conductivity of PE at different states. We also predict that amorphous PE may be super thermally conductive if chains are strictly stretched along heat flux.

Keywords Thermal conductivity; Molecular dynamic simulation; Polyethylene; Chain configuration

Citation: Zhang, X.; Wang, Y.; Xia, R.; Wu, B.; Chen, P.; Qian, J. S.; Liang, H. J. Effect of chain configuration on thermal conductivity of polyethylene—a molecular dynamic simulation study. *Chinese J. Polym. Sci.* <https://doi.org/10.1007/s10118-020-2466-y>

INTRODUCTION

Thermally conductive polymers get more and more attention in recent years, which are applied in many fields as thermal management material. Especially, for electric devices with coarse surfaces and/or aerospace devices that require light, soft and insulating thermal management materials, polymers are essential and irreplaceable by metals and ceramics. There are two kinds of thermally conductive polymers. One is filled polymer composite by mixing inorganic thermally conductive fillers into the polymer matrix. The other is polymer bulk, most of which are intrinsically high-thermally conductive. Usually, filled thermally conductive polymer composites are particularly concerned, because the polymer composites are easy to be fabricated and thermal conductivity of polymer composites can be readily improved by thermally conductive fillers. Researchers have tried various kinds of thermally conductive fillers such as metal, metal oxide, ceramic, carbon materials that may be one-dimensional particles, two-dimensional sheets, or three-dimensional crystal whiskers.^[1–8] However, there are still many challenges for the application of these thermally conductive polymer composites. Firstly, the filler needs to be functionalized before mixed into the polymer matrix.^[9–11] Secondly, filler-loading will increase the density and hardness of polymer

composites, which may damage the mechanical performance of polymers. Thirdly, present technologies to orientate anisotropy fillers in polymer matrix to get high thermal conductivity for polymer composites are complex and highly costly, which cannot be applied in massive production.^[12] So, it is worth considering other choices to make thermally conductive polymers.

Thermal conductivity of most polymers bulks is on the order of 0.1 W/mK, which is usually thought to be intrinsically thermal insulating. For instance, thermal conductivity of polyethylene (PE) bulk is about 0.2–0.5 W/mK.^[13–15] However, researchers found that PE chain may exhibit excellent thermal conductivity at stretching states. Theoretically, Henry and Chen found that an individual PE chain may have extremely high thermal conductivity or even divergent.^[16] Experimentally, researchers measured thermal conductivity of ultra-drawn PE nanofibers and got values about 104 W/mK that is far beyond thermal conductivities of many metal and ceramic materials.^[17] This means polymers may be intrinsically high-thermally conductive if the chains configuration are well arranged.

Researchers have carried out a series of research on thermal conductivity of PE chain. Various effects on thermal conductivity of PE chains such as dimensions, segment distribution, chain branching, chain twisting, etc. have been theoretically studied.^[18–22] PE bands are experimentally drawn to get fibers that show ultra-high thermal conductivity, though they are much lower than that of theoretical prediction.^[23,24] Up to now, some important questions are still open for these

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Received April 19, 2020; Accepted June 4, 2020; Published online July 30, 2020

intrinsically thermally conductive polymers. For instance, polymer crystal with orderly arranged chain segments in crystalline cells should have excellent thermal conductivity, whereas a high crystalline degree of polymer does not mean high thermal conductivity. Some researchers account for the phonon scattering at the interface of crystal and amorphous zones, but the stretched PE fibers exhibit excellent thermal conductivity though the interfacial scattering effect remains.^[25] There is a large difference between theoretically predicted ultra-high thermal conductivity of PE chain and experimentally measured relatively low thermal conductivity of PE fiber and bulk. Could it be possible to make a PE bulk with thermal conductivity as high as that of a single stretched PE chain?

In this study, we performed a molecular dynamic simulation on PE to study the effect of chain configuration on thermal conductivity. Firstly, we analyzed the stretched PE chains under different conditions, and then compared those thermal conductivities at different crystalline states. Typically, we considered the effect of the arrangement of polymer crystalline cells on thermal conductivity. We also compared continuous and fractured interfaces on affecting thermal conductivity of polymers. Our simulation study showed that the heat transports predominately along the chain, so good alignment of polymer chains is the key to produce a highly thermally conductive polymer.

MODEL AND SIMULATION DETAILS

Polyethylene chains were constructed by covalently bonded methylene groups ($-\text{CH}_2-$) with methyl ends using Material Studio.^[26] Polymer Consistent Force Field (PCFF) was applied to depict these PE chains as in reference.^[27] The molecular dynamic simulation was carried out using the large-scale atomic/molecular massively parallel simulator (LAMMPS).^[28] In each simulation, the model system was relaxed firstly in NVT (constant number of atoms, temperature, and volume) ensemble at 300 K, and then in NVE ensemble (constant number, temperature, and energy) to ensure the system reaches equilibrium. For PE with the predetermined crystalline degree, we made multi-steps equilibration to keep crystalline cells undisturbed while amorphous chains being well relaxed. The crystalline degree of PE bulk may be defined using the order parameter S .^[29]

$$S = \frac{1}{N(n-2)} \sum_{m=1}^n \sum_{i=3}^n \frac{3\cos^2\theta - 1}{2}$$

where N is the number of chains of polyethylene, n is the number of methylene groups, and θ is the angle formed by the two spaced carbon atoms on the chain along with the long axis of the chain. In this work, the crystallization was simulated in a homogeneous nucleation way, that is, polymer chains assembled into an ordered zigzag arrangement.

To calculate thermal conductivity of stretched chains and bulk of PE, we performed Non-Equilibrium Molecular Dynamic simulation (NEMD) for the equilibrated system.^[30–32] The spectrum of vibrational density of states (VDOS) is used to characterize the thermal transporting of polymers at different states as in references.^[20,21,33]

RESULTS AND DISCUSSION

Thermal Conductivity of Stretched PE chain

Firstly, we considered thermal conductivity of stretched polymer chains. As in experimental and theoretical studies, super stretched PE chains exhibit excellent thermal conductivity far more beyond that of thermal conductivity of PE bulk. Previous studies showed that various chain properties, such as the morphology, branching, torsion, etc., may depress thermal conductivity of PE in bulk.^[19,21] Besides these factors, we consider that the physical interaction between adjacent chains in bulk may affect the heat transporting along polymer chains as well. So, we compared an independent PE chain and two adjacent PE chains in Fig. 1 to study the effect of physical interaction on thermal conductivity of aggregated polymer chains. In Fig. 1(a), we constructed fully stretched chains with two ends fixed same as in references.^[33,34] Here, a fully stretching state means that PE chain is constructed as an ideal zigzag conformation with the minimum energy, and then two methyl ends of the chain are physically fixed. To equilibrate the PE chain, the methylene groups in PE chain are relaxed in NVT (300 K) and NVE ensembles subsequently. Two adjacent chains are constructed with the intra-chains spacing of 4 Å, which makes adjacent chains able to physically repel each other during random Brownian motion. The corresponding thermal conductivity values of stretched chains are shown in Fig. 1(b). The same as in references,^[33,34] the thermal conductivity of stretched independent chain increases with the increase of chain length (number of methylene groups). Typically, the thermal conductivity of stretched PE with 100 methylene groups is about 15 W/mK, and for that with the chain length about 800 methylene groups, the thermal conductivity is about 40 W/mK. However, thermal conductivities of two adjacent chains are obviously lower than those of independent chains as shown in Fig. 1(b). We calculated the vibrational density of states (VDOS) of the independent PE chain and adjacent PE chains. Typical VDOS spectra of PE chains with 200 methylene groups are shown in Fig. 1(c), in which the VDOS spectrum of two adjacent chains show the lower peaks at frequencies of 19 and 37 THz compared to that of the independent chain. In Fig. 1(d), VDOS curves of individual chains (Chain 1 and Chain 2, respectively) of two adjacent chains exhibit different peaks at about 1, 10, and 24 THz, etc. We think the inconsistency of VDOS curves of individual chains of two adjacent chains means two individual chains vibrate at different frequencies and the methylene groups in either chain may collide against the groups at the other chain to exchange energy, which causes energy transporting between chains other than along chains. As a result, thermal conductivity of adjacent chains is lower than that of the independent chain. It is worthy to be noted that thermal conductivity values of adjacent chains do not reduce with the increasing number of adjacent chains in the cases that there is no other intra-chain interaction.

Secondly, polymer chains are naturally coiled in bulk, which is different from those at fully stretched state. Previous studies showed that the stretching ratio of chains strongly affects thermal conductivity of the polymer. We compared thermal conductivities of two interacting adjacent chains with different stretching ratios. The schematic morphologies of str-

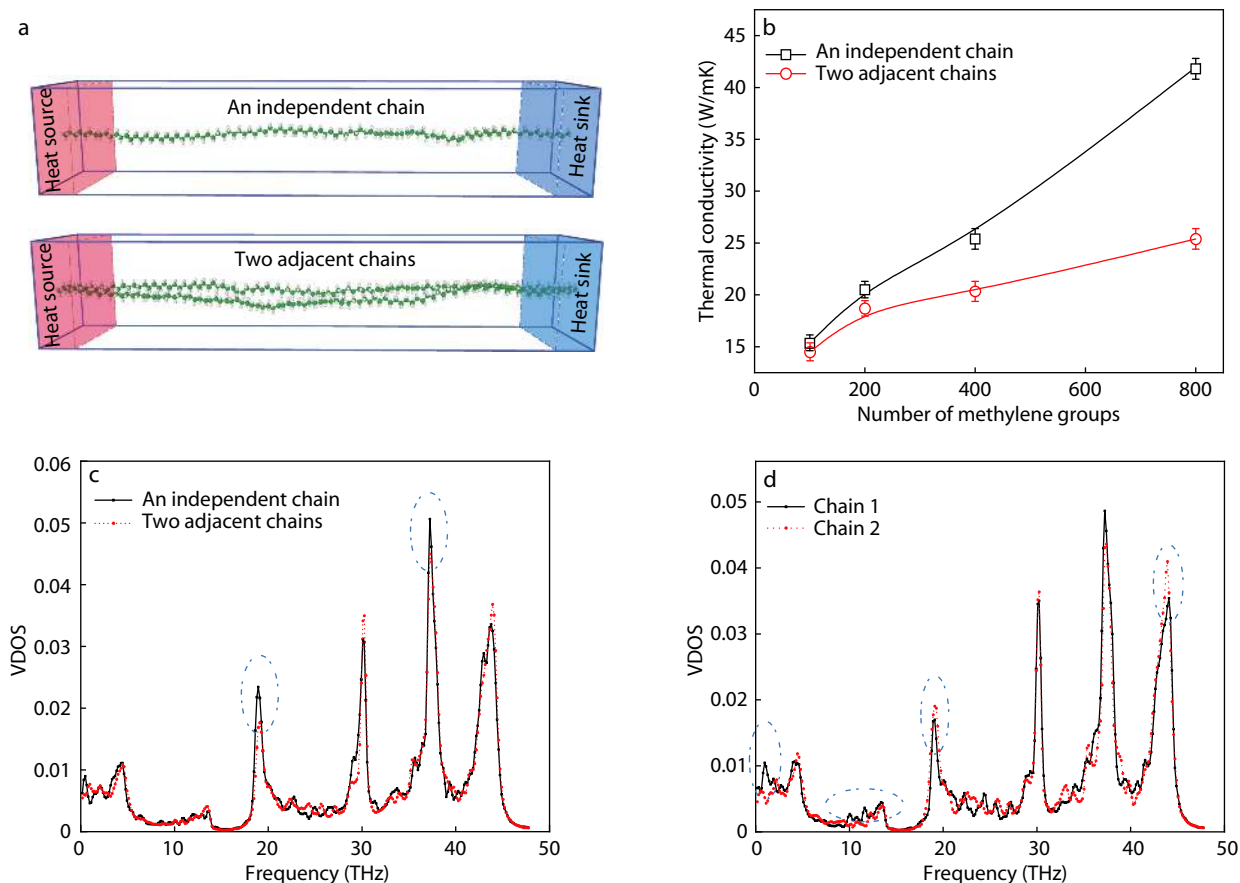


Fig. 1 Thermal transport along a single independent chain and interacting adjacent chains at stretched state. (a) Simulation model for an independent chain and two adjacent chains at stretched state. (b) Thermal conductivity of stretched PE chains with varied chain lengths (number of methylene groups). (c) VDOS of an independent PE chain and two adjacent PE chains. (d) VDOS of individual chains (Chain 1 and Chain 2) of two adjacent chains.

etched interacting chains are shown in Fig. 2(a). It is found in Fig. 2(b) that thermal conductivity of polymer decreases with the stretching ratio decreasing, especially when stretching ratio decreases from 1 to 0.95. The VDOS shown in Fig. 2(c) also testifies the low thermal conductivity of less stretched chains, in which the VDOS peaks (at about 1, 4, 19, 30, and 37 THz) of chains with 0.7 stretching ratio are obviously lower than those of fully stretched chains (1.0 stretching ratio).

Our studies on stretched chains show that, owing to the mutual interference effect between adjacent chains and low stretching ratio of chains in bulk, thermal conductivity of PE bulk is far lower than that of independent PE chain. It is impossible to make a polymer bulk with thermal conductivity the same as that of a single independent chain.

Thermal Conductivity of Polymer Crystals

As is well known, crystallization improves the order of polymer chains. However, crystalline polymers such as PE does not show high thermal conductivity in crystalline bulk. Here, we study the effect of crystalline configuration of polymer chains on thermal conductivity. We firstly constructed a simple PE crystal composed of 16 PE chains each having 200 methylene groups as shown in Fig. 3(a). The crystalline degree of the PE crystal is realized by relaxing some segments of chains, which is

characterized using the order parameter S . Such model is similar to experimentally super-drawn fibers, in which PE chains are orderly aligned in crystalline zones along with the long axis of the fiber. We testified the validity of order parameter S by calculating the energy and density of PE bulk. In Fig. 3(b), system energy decreases along with the increasing order of parameter S , especially when S values are 0.4, while the density of the PE bulk increases correspondently. This means the order parameter S can reflect energy minimization and density increasing of PE in crystallizing. So, we use S value to represent crystalline degree of PE bulk. We calculated thermal conductivity of PE crystal fiber along with chain extension direction, which is the long axis of PE fiber as shown in Fig. 3(a). In Fig. 3(c), thermal conductivity of PE fiber increases almost exponentially with the increase of the order parameter S , that is, the increase of crystalline degree. However, the thermal conductivity of PE crystal is far lower than that of the independent stretched chain (21 W/mK, 200 methylene groups), even for the perfect crystal with the order parameter S of 1 (18 W/mK). This is owing to the mutual interfering effect from adjacent chains as discussed in the above section.

Usually, crystalline cells in the polymer are randomly arranged, which is known as the polycrystalline state. In

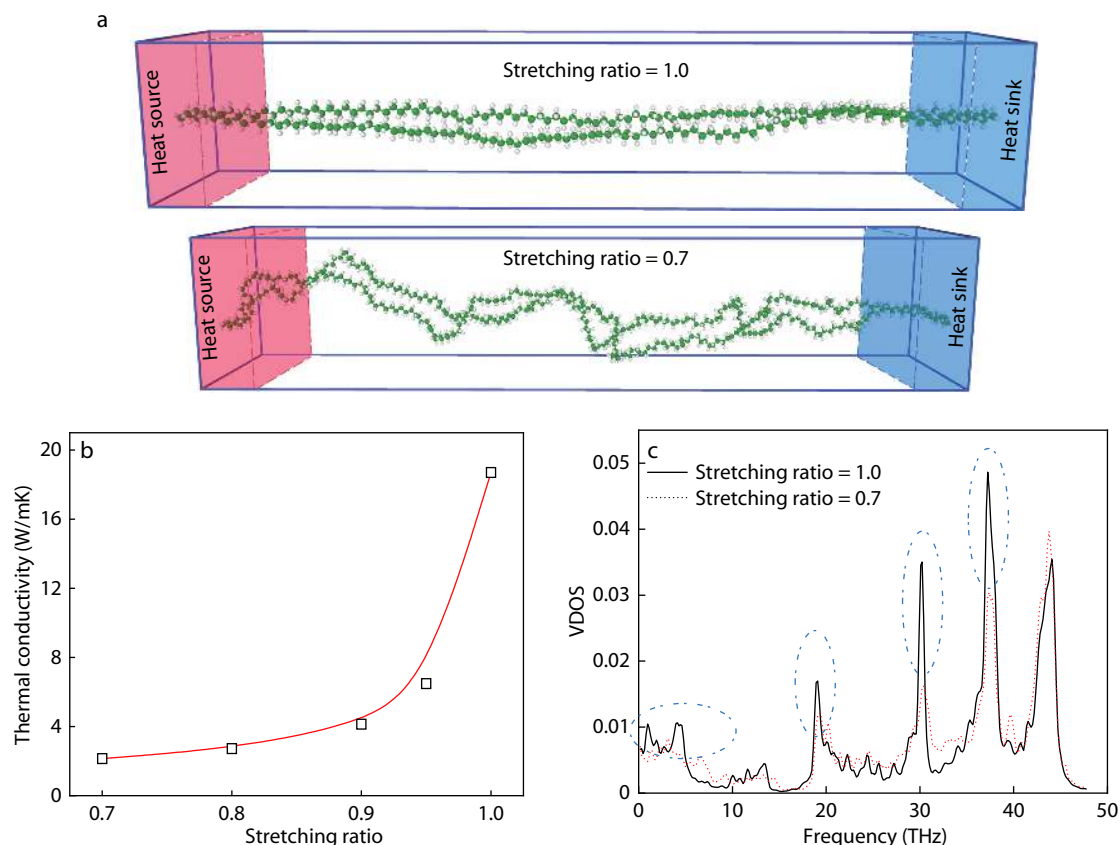


Fig. 2 Thermal conductivity of stretched PE chains at different stretching ratios. (a) Representative morphologies of stretched interacting chains. (b) Variation of thermal conductivity with stretching ratio. (c) VDOS of the PE chains with the stretching ratios of 1.0 and 0.7.

Fig. 4(a), we construct four crystalline PE bulks with the order parameter S (crystalline degree) being 0.45, and each crystalline bulk has two crystalline cells deliberately arranged into varied angles. In each crystalline cell, PE chains are parallel to the long axis of the crystalline cell. We calculated thermal conductivity of crystalline PE bulks along with one selected crystalline cell as shown in Fig. 4(a), and the corresponding thermal conductivity values are shown in Fig. 4(b). It is obvious that crystalline polymer exhibits good thermal conductivity only in the case of polymer chains in both crystalline cells parallel to the thermal transporting direction, that is, 0° in Fig. 4. This means crystallization contributes to polymer thermal conductivity only in the cases of thermal transporting along the chain.

To clearly show the difference of thermal transporting along the covalent chain and across adjacent chains (intra-chains), we constructed a PE crystal cell composed of 16 PE chains of 200 methylene groups as shown in Fig. 5(a). In this crystal cell, the PE chain segments are stacked into parallel slices. We tested thermal transporting in the cases of heat flux being parallel and vertical to the PE chains. We also changed the pairwise interaction to compare the effect of pairwise interaction between elements on thermal transporting along the chain and intra-chains. The PCFF potential used in Lamps employed a Lennard-Jones potential to depict pairwise interaction.

$$E = \varepsilon \left[2 \left(\frac{\sigma}{r} \right)^9 - 3 \left(\frac{\sigma}{r} \right)^6 \right] \text{ at } r < r_c$$

In this expression, ε is energy amplitude, σ is equilibrate distance between adjacent elements, and r_c is the cutoff of pairwise interaction.

Here, we changed the energy amplitude value ε' from 0.5 time to 2 times of ε_0 (initial value of pairwise interaction setting in PCFF). As shown in Fig. 5(b), thermal transporting along the covalent chain is obviously faster than that of intra-chains; the latter is less affected by pairwise interaction while thermal transporting along the chain increases linearly with pairwise interaction increasing.

Shortly, our simulation study on crystalline PE shows that thermal transporting prefers along the chain rather than across adjacent chains no matter if the chains are crystallized. Polymer crystal cells may exhibit good thermal conductivity only in the case that thermal transporting is along the chain extension direction in the crystal cell. In a polycrystalline polymer bulk, crystal cells are isotopically dispersed, which breaks down thermal transporting pathways and depresses thermal conductivity of the crystalline polymer. So, the polycrystalline PE does not show excellent thermal conductivity. Experimental studies have revealed that thermal conductivity of polymer chains strongly relies on the chain orientation rather than crystallization.^[35] Zhu *et al.* found that stretched PE microfibers with a low crystalline degree (83%) show better

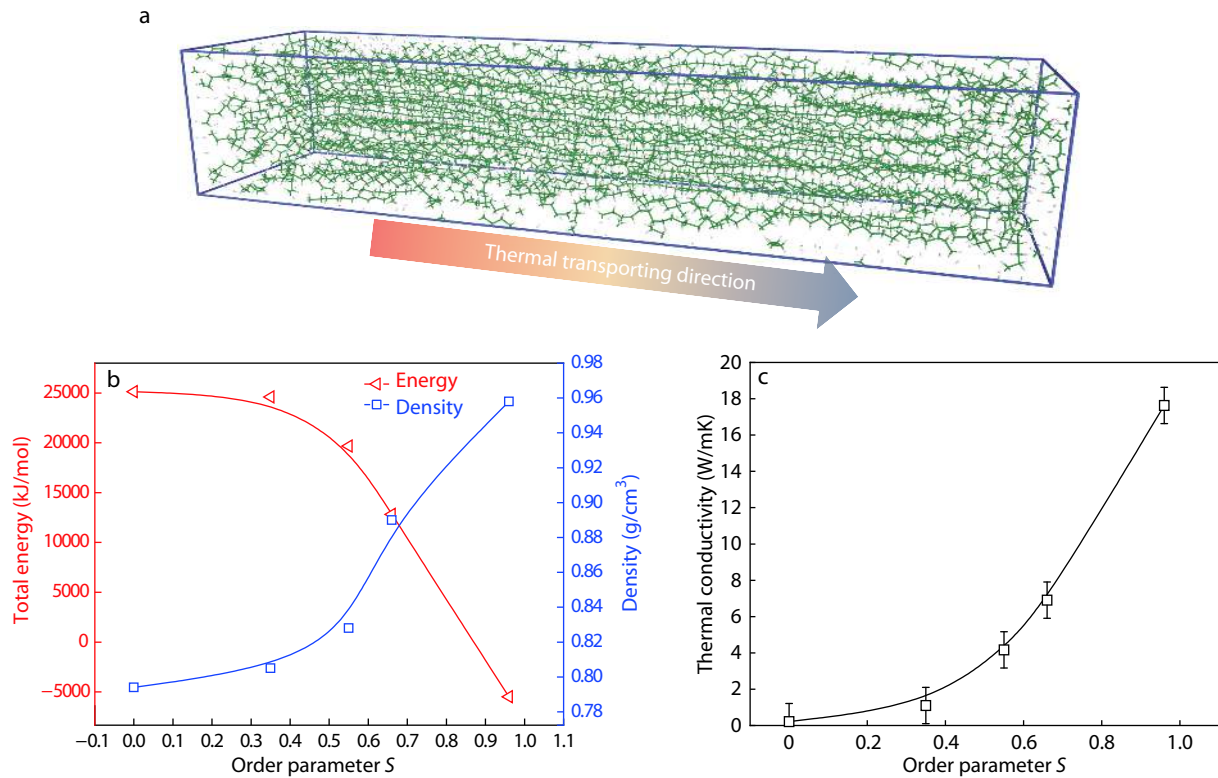


Fig. 3 Thermal conductivity of PE crystals. (a) Simulation model of PE crystal. (b) Variation of energy and density along with the order parameter S . (c) Thermal conductivity of PE crystal along with the order parameter S .

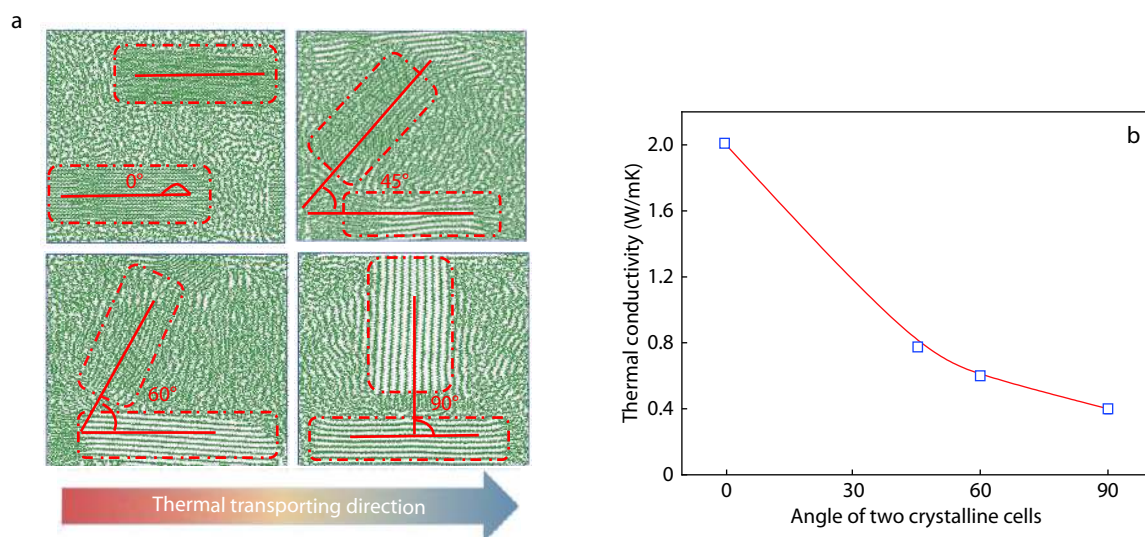


Fig. 4 Thermal conductivity of polycrystalline PE bulk. (a) Four arrangements of crystalline cells in PE bulk. (b) Thermal conductivity of PE crystals.

thermal conductivity than those with a high crystalline degree (92%).^[36] This can be readily explained by our model: because amorphous PE chains are easier to be oriented than those in crystalline cells, at the same stretching ratio there are more chains in low crystalline samples being oriented than those in a high crystalline sample.^[36] This is the same with a recent study on PE film, which shows that amorphous region of the PE bulk accounts for the high thermal conductivity of

stretched PE film, because non-crystalline chains are disentangled and well aligned in drawing process.^[24]

Effect of Intra-zone Chains on Thermal Conductivity of Polymer

Since most polymers are semi-crystalline, interfaces between crystal and amorphous zones are believed to affect thermal conductivity. We build two models with different interfaces between crystal-amorphous zones as shown in Fig. 6. For model

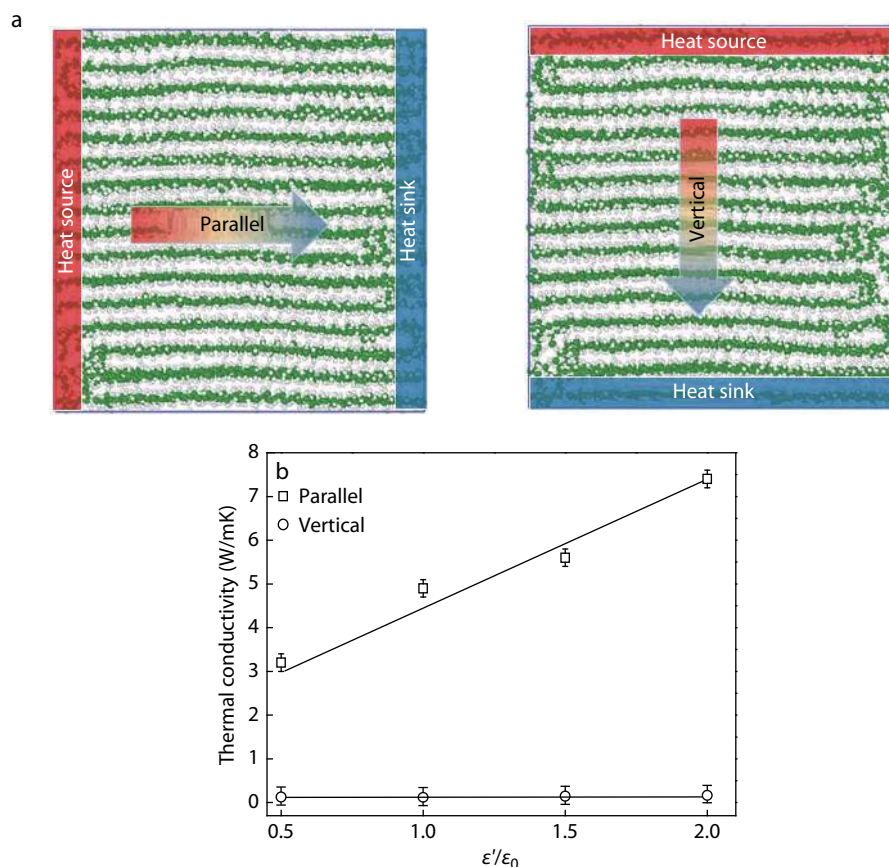


Fig. 5 Thermal conductivity of PE crystal cell. There are 16 PE chains involved into the crystal cell, each composed of 200 segments. (a) Thermal transporting along and vertical to the aligned chains in crystal cell. (b) Thermal conductivity of crystal cell with varied pairwise interaction.

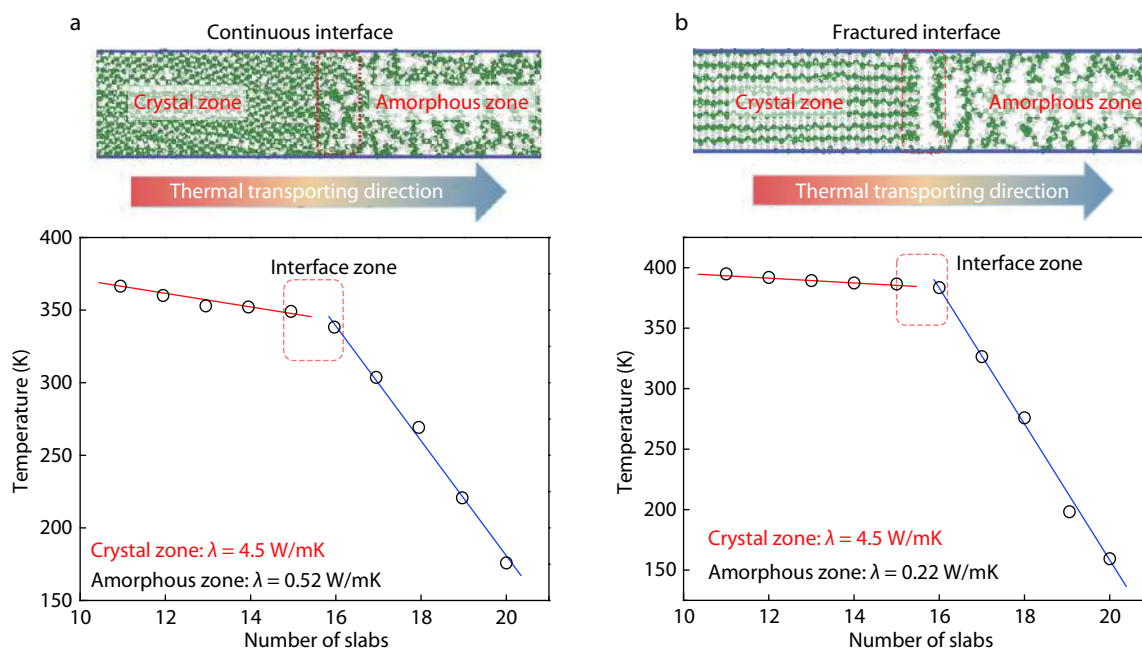


Fig. 6 Effect of inter-zone chains on thermal conductivity of crystalline PE. The PE bulk is composed of 16 PE chains that contain 200 segments each. Only part of the model is shown here for clarity. (a) Continuous interface in crystalline polymer. (b) Fractured interface in crystalline polymer.

with the continuous interface (Fig. 6a), there are polymer chains running through the crystal and amorphous zones, which we named intra-zones chains. For the model with the fractured interface (Fig. 6b), polymer chains are segregated from each other into either zone. In both models, temperature gradients clearly break down at interfaces, which are corresponding to the depression of thermal conductivity. However, the slopes of temperature gradient lines in amorphous zones of these two models are different. Thermal conductivity values of the amorphous zone with intra-zone chains (continuous interface model) are over 2 times of that without intra-zone chains (fractured interface model). This means intra-zone chains can decrease thermal resistance of the zones interface, which is similar to the effect of surface modification onto inorganic particle in a polymer matrix that is found to effectively improve thermal conductivity of polymer composites.^[37–39]

CONCLUSIONS

In this work, we studied the effect of chain configuration on thermal conductivity in stretched states and crystalline bulk. Thermal transporting is found mainly along the covalent chain. Interaction between adjacent chains dissipates the energy and depresses thermal transporting along the chain, so the thermal conductivity of PE bulk is always lower than that of independent PE chain. We checked thermal conductivity of PE under various crystalline conditions and found that crystalline cell of polymers with well aligned chains exhibits excellent thermal conductivity in the cases of thermal transporting along the chain. For semi-crystalline PE bulk, intra-zone chains are good for thermal transporting. Our simulation study predicts that well aligned polymer chains along thermal transporting direction are able to build highly thermally conductive polymer bulk in an amorphous state. This amorphous thermally conductive polymer is soft and light compared with the inorganic particles filled polymer composites, which is more suitable for weight sensitive devices such as in fields of aerospace, portable equipment and other applications.

ACKNOWLEDGMENTS

This work was financially supported by the National Key R&D Program of China (No. 2017YFB0406204), the National Natural Science Foundation of China (No. 51973002), and University Institution of High Performance Rubber Materials of Anhui Province.

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