To modulate thermal conductivity of poly(vinylidene fluoride) by electric fields

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ABSTRACT

Phonon engineering focusing on the heat transport modulation on the atomic scale has arisen in recent decades. In addition to the reported ways of phonon engineering like controlling material size, doping and mechanical stretching, in this work, we show that electric field can also modulate heat transport. Thermal conductivity of poly(vinylidene fluoride) (PVDF), one typical electroactive ferroelectric polymer, is investigated by molecular dynamics simulation. Interestingly, the electric-field-poled PVDF array shows higher thermal conductivity than that of unpoled one along all three directions, and the enhancement ratio approach 225% along the polarization direction. The morphology and phonon property analysis reveal that the enhancement of thermal conductivity arises from the higher inter-chain lattice order, stronger inter-chain interaction, higher phonon group velocity and suppressed phonon scattering in poled PVDF. Moreover, it shows that the enhancement is more obvious at lower temperature. Investigation on thermal conductivity versus electric field shows that the enhancement is transient after the field exceeds the threshold. Our study offers a new strategy of phonon engineering.

KEYWRDS: Phonon engineering; Thermal conductivity; Electric field poling; Poly(vinylidene fluoride); Molecular dynamics.
Introduction

Modulating the thermal conductivity of materials is significant for many applications, such as heat dissipation in electronics, thermal insulation and thermoelectric. Phonon engineering [1, 2] has been arisen in recent decades, which focuses on the modulation of heat transport by utilizing phonon properties such as wave effect [3], boundary scattering effect, low dimensional scattering effect [4] and anharmonic scattering effect [5]. Early works of phonon engineering mainly focus on modulating thermal conductivity of inorganic material and have made significant progress. However, with extensive use of polymers in flexible electronics, photovoltaic energy conversion and high power electronics [6-8], modulating thermal conductivity of polymers has become an urgent issue due to the low value of ~ 0.1 Wm$^{-1}$K$^{-1}$. Moreover, polymers with high thermal conductivity will replace traditional heat spreaders and heat exchanger, with superb features including structural compactness, light weight, anti-corrosion, and low-cost [9, 10]. Thus, how to modulate the thermal conductivity of polymers is becoming a new focus of phonon engineering.

The main strategies of phonon engineering in polymers include engineering morphology in micro/nanoscale and compositing highly thermal conductive fillers [6]. The methods of morphology engineering mainly include mechanical stretching [11, 12], nanoscale-templating [13-15], electrospinning [16, 17], cross-linking [18, 19], and π-π stacking [20]. Shen et al. [21] produced a polyethylene nanofiber with a 400 drawing ratio, obtaining a thermal conductivity of 104 Wm$^{-1}$K$^{-1}$. Xu et al. [22] fabricated polyethylene films with enhanced thermal conductivity of 62 Wm$^{-1}$K$^{-1}$ by aligning polymer chains. These works validated the theoretical prediction by Henry and Chen [23] on the high thermal conductivity of single polymer chain. For polymer nanocomposites, recent efforts are mainly focusing on reducing interfacial thermal resistance between fillers and polymeric matrix[19], as well as forming inter-filler network [6] to improve the thermal conductivity. Yu et al. [24] reported a thermal conductivity of 10 Wm$^{-1}$K$^{-1}$ of epoxy blended with covalent functionalized boron nitride. Huang et al. [25] reported a thermal conductivity of 7.3 Wm$^{-1}$K$^{-1}$ of epoxy by forming inter-connected network of graphene and carbon nanotube.

Electric field has been used to modulate physical properties of materials, such as electronic band gap [26], electrical superconductivity [27], magnetic skyrmions [28] and nonlinear optical susceptibility [29]. Modulations with electric field have the advantages of in situ, flexible control of
magnitude and direction, quick response and low power consumption [30-32]. Electric field has been used to align fillers in polymer composites such as graphene and boron nitride flakes [33, 34], forming a chain-like network structure in polymer matrix, improving thermal conductivity along electric field direction. However, forming a network requires high filler concentration, which could compromise mechanical, electrical, and optical properties. **It will be much better if electric field could modulate intrinsic thermal transport of polymers without fillers, which is still an open question.**

Poly(vinylidene fluoride) (PVDF) is a typical ferroelectric material [35]. It’s reported that β-phase of PVDF can be poled by electric field [36]. The outstanding electroactive characteristic has been exploited for a wide variety of applications, including biomedicine [37], energy storage [38], sensors and actuators[39]. Recently, Dong et al. [40] proposed phonon renormalization induced by electric field in P(VDF-TrFE). However, their model is focused on single polymer chain and the electric field applied is along the chain, while electric field applied in most applications is along the inter-chain direction. **Thus, how can the electric field influence heat transport in PVDF, need more investigation.**

In this work, the electric field effect on thermal conductivity of β-phase PVDF is investigated **numerically.** Firstly, the thermal conductivities of both amorphous PVDF (A-PVDF) and chain arrays are calculated by MD simulations. In order to study the effect of electric field, two kinds of array structure, unpoled array-PVDF (UA-PVDF) and poled array-PVDF (PA-PVDF) are investigated and compared. The mechanism of electric field effect on thermal transport is discussed by comparing phonon properties and chain’s morphology. Lastly, the dependence of thermal conductivity of UA-PVDF on electric field is simulated and discussed.

**Method and model**

The equilibrium molecular dynamics (EMD) simulation method is used to calculate the thermal transport properties [7, 41]. All EMD simulations in this work are performed by the large-scale atomic/molecular massively parallel simulator (LAMMPS) package [42]. The interactions between atoms are described by the polymer consistent force field (PCFF) [43] which includes anharmonic bonding terms and is intended for applications in polymers and organic materials. Periodic boundary conditions are applied in all three dimensions. And the velocity Verlet algorithm is employed to integrate equations of motion [44]. 0.25 fs and 10 Å are chosen as time step and cutoff distance for
the Lennard-Jones interaction, respectively. In addition, 5 independent simulations with different initial conditions are conducted to get better average. (MD simulation details are given in the Supplementary Material.)

![Diagram](image)

**Figure 1.** Schematics of structure of (a) amorphous PVDF (A-PVDF), (b) unpoled array-PVDF (UA-PVDF), and (c) poled array-PVDF (PA-PVDF).

**The structures of A-PVDF, UA-PVDF and PA-PVDF are shown in Figure 1.** A-PVDF is constructed by randomly packing 40 coiled PVDF chains into a box [45] (detailed constructing processes are given in the Supplementary Material). For the PVDF array, the initial structures are constructed by aligning 40 straight PVDF chains in an orthogonal lattice, with periodic boundary conditions applied in all three spatial directions. For UA-PVDF, as shown in Figure 1(b), half of chains
orientate oppositely with the other half of chains along \( y \) direction (direction of dipole moment), the dipole moments of two parts cancel each other out, resulting in a zero dipole moment of the whole system. For PA-PVDF, as shown in Figure 1(c), the orientations of all chains along \( y \) direction are the same, generating a net dipole moment of the whole system. Subsequently, these structures are simulated in NPT ensembles at target temperatures and 1 atm for 100 ps to obtain the optimized structures and simulation cell sizes, then followed by NVE ensembles for 100 ps before collecting heat flux of all three directions (inter-chain direction \( x \) and \( y \), along-chain direction \( z \)) in NVE ensembles for 4 ns.

**Results and discussion**

**Firstly, the thermal conductivity of A-PVDF is studied.** The value is obtained as 0.22 ± 0.01 Wm\(^{-1}\)K\(^{-1}\) at room temperature, which is the same with the reported experimental value of 0.22 Wm\(^{-1}\)K\(^{-1}\) [46]. This value is also similar to that of bulk epoxy [19], cross-linked PE [47] and hydrogel [48]. In addition, it is calculated that thermal conductivity of A-PVDF has no dependence on temperature in the range from 300 K to 600 K, as shown in Figure S2(a). The phonon density of states (PDOS) is calculated to explain the temperature-independent thermal conductivity, which is shown in Figure S2(b). There is little difference between the PDOS at 300 K, 400K and 500 K along all three directions, which indicates that high temperature cannot introduce extra phonon scattering in such an amorphous system that already encompasses numerous phonon scattering, resulting in similar thermal conductivities at different temperatures.

**Then, the thermal conductivity of UA-PVDF and PA-PVDF are investigated.** Before studying the thermal conductivity, the simulation cell size is checked to overcome the finite size effect. (Details are given in the Supplementary Material.) The integrals of HCACF along \( x \), \( y \), and \( z \) directions for two types of two structures at 300K are shown in Figure S4, which demonstrate the anisotropic thermal transport. For UA-PVDF, integral of HCACF converges to 0.16, 0.16, and 24.2 Wm\(^{-1}\)K\(^{-1}\) along \( x \) (inter-chain direction perpendicular to the polarization direction), \( y \) (inter-chain direction parallel to the polarization direction) and \( z \) (along-chain) directions, respectively. For PA-PVDF, integral of HCACF converges to 0.36, 0.52, and 31.5 Wm\(^{-1}\)K\(^{-1}\) along \( x \), \( y \) and \( z \) directions, respectively. The anisotropic thermal transport is due to the strong covalent bonds along the chain but weak non-bonded interactions along the inter-chain directions. Compared with UA-PVDF, \( \kappa_x \), \( \kappa_y \), and \( \kappa_z \) of PA-PVDF are
increased by 125%, 225% and 30%, respectively. This result indicates that by inducing polarity to the structure, the inter-chain thermal transport (especially along the dipole direction) can be largely enhanced. This improvement is attributed to the changes in structure morphology and phonon properties as will be discussed later.

**Figure 2 shows the temperature dependence of thermal conductivities of two array structures.** The investigated temperature range is 300 K to 500 K. It is noted that 500 K is higher than the melting point of amorphous PVDF measured experimentally. Because the structure is crystal and the molecular chains are assumed to be infinitely long in EMD simulations, resulting in infinite molecular weights and a higher melting point [45, 49, 50]. For PA-PVDF, the thermal conductivity reduces as temperature increasing. The typical temperature dependence of thermal conductivity in perfect crystal as $T^{-1}$ induced by Umklapp phonon-phonon scattering is plotted as a reference. As can be seen, the decreasing trend of thermal conductivity in PA-PVDF is slightly sharper than the reference line. This is because the morphology changes in polymers are severer than that in perfect crystal at higher temperature[7], which would increase phonon anharmonicity and suppress thermal conductivity. On the other hand, for UA-PVDF, $\kappa_z$ shows a decreasing trend, but $\kappa_x$ and $\kappa_y$ are temperature independent in the range from 300 K to 500 K. Moreover, the enhancement in thermal conductivity induced by structure poling becomes lower at higher temperature, and almost disappears at 500K.

![Figure 2](image-url)

**Figure 2.** Temperature dependence of thermal conductivity of UA-PVDF and PA-PVDF along directions of (a) $x$; (b) $y$ and (c) $z$. 
To study the thermal conductivity enhancement induced by electric polarization, the structure morphology is investigated. Stable supercell structures after relaxation at 300K for the two structures are shown in Figure 3. Along z direction, all molecular chains are still arranged in a form of array, no obvious along-chain morphological difference is observed between the two structures. The strong covalent bonds dominate the along-chain heat transport, generating high $\kappa_z$ of both structures. And this good alignment also gives $\kappa_z$ the negative temperature dependence which is typical in crystal materials. However, there is a significant discrepancy in inter-chain morphology between UA-PVDF and PA-PVDF. As can be seen in Figure 3(a), for UA-PVDF, the orientations of molecular chains along $x$ and $y$ directions are inconsistent. Each molecular chain rotates at different angles around its own carbon skeleton, resulting in a different dipole direction of each chain. The inter-chain arrangement of the relaxed structure is more disordered than the initial structure, which can be regarded as an inter-chain amorphous state. The inter-chain disorder can induce numerous phonon scattering[49], thus resulting in low $\kappa_x$ and $\kappa_y$ of unpoled structure, as well as the independence of inter-chain thermal conductivity on temperature. On the contrary, for the relaxed PA-PVDF structure, as shown in Figure 3(b), the orientations of all molecular chains along $x$ and $y$ directions are highly consistent. The inter-chain structure is highly ordered, which is in an inter-chain crystalline state. Thus, the scattering of phonons is largely reduced when it’s transporting across molecular chains, resulting in an improved $\kappa_x$ and $\kappa_y$ of PA-PVDF.

To better show the morphology change, radial distribution function (RDF) of carbon and fluorine atoms are furtherly calculated to quantify inter-chain orders for UA-PVDF and PA-PVDF at different temperatures. (Details of calculating RDF are given in the Supplementary Material.) The RDF results of carbon atoms at 300K are shown in Figure 3(c). At 300 K, there are significant changes of UA-PVDF compared with those of PA-PVDF. First, peaks around 8 Å and 12.5 Å are disappeared, indicating the decrease of inter-chain lattice order. Second, peaks shifting to the right, suggesting the increase of the inter-chain distance. As a result, the inter-chain nonbonding interactions which are mainly responsible for the inter-chain heat transfer become weaker, resulting in suppressed $\kappa_x$ and $\kappa_y$ of UA-PVDF. The increasing inter-chain distance will also create more space for chain bending and rotation, and induce scattering of phonons transporting along the chain, which might be responsible for the slightly lower $\kappa_z$ of UA-PVDF. Third, the sharp peaks are flattened and their widths are broadened, indicating the increasing inter-chain motion range and weaker constraining force.
of atoms, which means soften of phonons. Phonon softening effect would reduce phonon frequencies and group velocities [51], thus suppressing inter-chain thermal conductivities of the unpoled structure. When temperature rises to 500 K, as can be seen in Figure S5(a), discrepancy between two structures becomes much small, explaining the similar thermal conductivities of two structures at 500K. The RDF of fluorine atoms presented in Figure S6(a) also shows the same tendency.

Figure 3. Structures after relaxation of (a) UA-PVDF; (b) PA-PVDF at 300 K; (c) Radial distribution function of carbon atoms; (d) mean square displacement of carbon atoms.

To further describe the different inter-chain interactions between UA-PVDF and PA-PVDF, mean square displacement (MSD) of carbon atoms at 300K are calculated. As can be seen in Figure 3(d), MSD of carbon atoms along y direction of PA-PVDF are obviously reduced compared with that of UA-PVDF, and MSD along x direction presented in Figure S6(b) also shows the same tendency, which means stronger inter-chain interactions in PA-PVDF. Therefore, the inter-chain thermal transport in PA-PVDF is more efficient. Moreover, in PA-PVDF, MSD along y direction is
smaller than that along $x$ direction, which could explain the larger $\kappa_y$ compared with $\kappa_x$. While in UA-PVDF, discrepancy of MSD along $x$ and $y$ directions is unobvious, which could explain the similar $\kappa_x$ and $\kappa_y$. Besides, along $z$ direction, MSD is the smallest because the strong covalent bonds along chain, and MSD of PA-PVDF shows a slight decrease compared with that of UA-PVDF, which might be responsible for the slightly higher along-chain thermal conductivity of PA-PVDF. The MSD of fluorine atoms presented in Figure S6(b) also shows the same tendency.

To gain further understanding of the polarization effect on thermal conductivity, the spectral energy density (SED) is calculated to qualitatively analyze the difference in heat conduction between two structures. SED at 300K in the full-frequency range is given in Figure S7. Keeping in view that dominant thermal energy carriers in crystalline polymers are usually low-frequency phonons [50], enlarged SED contour maps in the frequency range below 10 THz along all three directions of UA-PVDF and PA-PVDF at 300K are presented in Figure 4. For SED along $\Gamma$ - $Y$ ($y$ direction), obvious changes between UA-PVDF and PA-PVDF can be observed. As denoted by white dashed ellipses, along the direction from the Brillouin zone edge to the center, the acoustic phonon branches of PA-PVDF exhibit clear spectra, whereas those of UA-PVDF show severe broadening and can’t be figured out when frequency is over 0.5THz. This phonon broadening effect would introduce more phonon scattering, resulting in smaller phonon lifetimes [52]. Additionally, curves of these branches of PA-PVDF are steeper than those of UA-PVDF, indicating higher phonon group velocities in PA-PVDF. These two effects contribute to the improved $\kappa_y$ in PA-PVDF. Similar changes are also observed in SED profile along $\Gamma$ - $X$ ($x$ direction). Additionally, it is noticed that the inter-chain SED profile of PA-PVDF becomes fairly flattened when frequency surpasses 2 THz, indicating that high frequency phonons hardly contribute to the inter-chain thermal transport. This flattened shape can be also observed in the inter-chain phonon dispersion of polyethylene [53], which is caused by the weak vdW interactions between polymer chains. For PA-PVDF, phonon group velocities of branches in white dashed ellipses along $\Gamma$ - $Y$ direction are higher than those along $\Gamma$ - $X$ direction, and there existing extra phonon branches along $\Gamma$ - $Y$ direction as donated by white solid ellipses. Thus, $\kappa_y$ are higher than $\kappa_x$ in PA-PVDF. For SED along $\Gamma$ - $Z$ ($z$ direction), phonons in UA-PVDF and PA-PVDF have much higher group velocities than those along other two directions, resulting a large value of $\kappa_z$ in both structures. Meanwhile, compared with UA-PVDF, the dispersion curves along $\Gamma$ - $Z$ of PA-PVDF is apparently slenderer, indicating the longer phonon lifetimes, which
results in higher along-chain thermal conductivity of PA-PVDF.

**Figure 4.** SED maps of PA-PVDF along (a) $\Gamma - X$, (b) $\Gamma - Y$ and (c) $\Gamma - Z$ at 300K; and of UA-PVDF along (d) $\Gamma - X$, (e) $\Gamma - Y$ and (f) $\Gamma - Z$ below 10 THz at 300K.
When temperature rises to 500 K, as shown in Figure S11, along the direction of Γ – X and Γ – Y, phonon branches at 500 K of PA-PVDF become more indistinct compared with that at 300 K, indicating stronger inharmonic phonon scattering. Moreover, PDOS at low frequency presented in Figure S8 shows blue shift, which indicating the decrease of phonon group velocity. Thus, $\kappa_x$ and $\kappa_y$ of PA-PVDF show dramatic decrease. However, for UA-PVDF, SED maps along these two directions shows no obvious discrepancy, resulting in similar $\kappa_x$ and $\kappa_y$ at two temperatures. Along Γ – Z, phonon branches of both PA-PVDF and UA-PVDF become broader at 500 K, which means severer inharmonic phonon scattering, resulting decreased $\kappa_z$ of both structures. In addition, SED shapes of two structures along Γ – Z are quite similar at 500 K, which could explain their similar $\kappa_z$ at that temperature.

To further illustrate the feasibility of electrical polarization, external electric field along $y$ direction is applied to the UA-PVDF. When electric field is applied, UA-PVDF is simulated in NPT
ensembles at 300K and 1 atm for 100 ps, followed by NVE ensembles for 100ps. Then the electric field is removed, followed by the same steps that is used to calculate thermal conductivities. The relaxed structure after simulation in electric field of 1.2 GV/m is shown in Figure 5(a). As a result, the morphology of UA-PVDF is significantly changed by this electric field. All molecular chains and electric dipoles orient well along the direction of electric field, the inter-chain lattice order is largely improved, indicating the polarization of system. The action of molecular chain rotation can be observed in the attached video. The calculated $\kappa_x$, $\kappa_y$ and $\kappa_z$ versus electric field intensity are shown in Figure 5(b), 5(c) and 5(d), respectively. The threshold electric field for polarization is about 0.8 GV/m, which is consistent with the value of other numerical simulations [54, 55] and the experimental results of ultrathin P(VDF-TrFE) films [56, 57]. When electric field intensity is below 0.8 GV/m, inter-chain thermal conductivities is the same with that of initial unpoled structure, and hardly change with electric field. However, the inter-chain thermal conductivities suddenly increase to the value of poled structure when electric field intensity exceeds 0.8 GV/m. This thermal conductivity switch behavior mainly origins from morphological mutation induced by electric field, which is corresponding to the polarization switching phenomenon in ferroelectric polymers [36, 58, 59].

**Conclusion**

In summary, we have performed MD simulations to investigate the electric field effect on the thermal transport in PVDF. Thermal conductivity of amorphous PVDF is $0.22 \pm 0.01 \text{Wm}^{-1}\text{K}^{-1}$ at room temperature, which is independent on the temperature. The array structure is proposed to improve to the thermal conductivity. When the structure has not been poled by electric field, the along-chain thermal conductivity rises to $24.2 \text{Wm}^{-1}\text{K}^{-1}$ at 300 K. However, the inter-chain thermal conductivity is still low, about $0.16 \text{Wm}^{-1}\text{K}^{-1}$ at 300 K. After being poled by electric field, thermal conductivities along all three directions are enhanced, and show negative temperature dependence. The thermal conductivity enhancement ratio along the polarization direction is the most significant, from $0.16$ to $0.52 \text{Wm}^{-1}\text{K}^{-1}$ at 300 K. As temperature increasing, the enhancement becomes weaker and almost disappears at 500K. By calculation RDF, MSD and phonon SED, we demonstrate that the enhanced thermal conductivity of poled structure rises from increased inter-chain lattice order, stronger inter-chain interaction, higher phonon group velocity and decreased phonon scattering. And these effects are much weaker at 500K, which explain the small discrepancy in thermal conductivity between these
two structures at higher temperature. Moreover, thermal conductivities of unpoled structure simulated in different electric field are calculated, and the results show that thermal conductivity could be enhanced only if electric field intensity exceed the threshold value, which is about 0.8 GV/m in our simulation. This strategy of phonon engineering has the advantages of in situ, flexible control of magnitude and direction, quick response and low power consumption. And it could not only be applied to thermal modulation of PVDF-based materials, but also be promising to other electroactive ferroelectric materials.

Acknowledgements

This work is financially supported by the Fundamental Research Funds for the Central Universities, HUST (No. 2019kfyRCPY045, 2019kfyRCPY126 and 2018KFYYXJJ052) and the National Natural Science Foundation of China (No. 51972126 and 51772108). The authors thank the National Supercomputing Center in Tianjin (NSCC-TJ) and China Scientific Computing Grid (ScGrid) for providing assistance in computations.

Competing financial interests: The authors declare no competing financial interests.
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Supporting Information

To modulate thermal conductivity of poly(vinylidene fluoride) by electric fields

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S1. The EMD simulation details.

All EMD simulation details are given in Table S1. Green–Kubo formula is a result of the linear response theory and the fluctuation dissipation theorem, which relates the heat flux autocorrelation with the thermal conductivity. Noting that $k_B$ is the Boltzmann constant, $V$ is the system volume, $T$ is the temperature, $\tau$ is the correlation time, $\tau_0$ is the integral upper limit of heat current auto-correlation function (HCACF), $E$ is total kinetic energy of the group of atoms, $N$ is number of total atoms, and the angular bracket denotes an ensemble average.

### Table S1. Parameter settings in MD simulation.

| Method       | EMD (Green-Kubo method) |
|--------------|-------------------------|
| Force field  | PCFF                    |
| Boundary conditions | $x, y, z$: p$p$p |

| Ensemble | Settings | Purpose          |
|----------|----------|------------------|
| NPT      | Time step (fs) 0.25 | Runtime (ns) 0.1 | Relax structure |
|          | Temperature (K) 300 | Pressure (atm) 0 |                |
| NVE      | Time step (fs) 0.1 | Runtime (ns) 0.1 | Relax structure |
|          | Temperature (K) 300 | Thermostat       | Nose-Hoover    |
| NVE      | Sample interval time (fs) 3 | Runtime (ns) 4 | Data process   |
|          | Correlation time (ps) 100 | Temperature (K) 300 |                |

| Recorded physical quantity | |
|-----------------------------|--|
| Temperature | $\langle E \rangle = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 = \frac{3}{2} N k_B T_{MD}$ |
| Heat flux | $\vec{J} = \frac{1}{V} \left[ \sum_i e_i \vec{v}_i + \frac{1}{2} \sum_i \vec{r}_{ij} (\vec{F}_{ij} \cdot \vec{v}_i) \right]$ |
| Thermal conductivity | $\kappa = \frac{V}{3 k_B T^2} \int_0^{\tau_0} \langle \vec{J}(0) \cdot \vec{J}(\tau) \rangle d\tau$ |
S2. Detailed constructing process of A-PVDF.

When constructing A-PVDF, a single PVDF chain containing 100 carbon atoms is simulated and equilibrated at 300 K for 1 ns to form a compacted particle. Then 40 of these particles are randomly packed into a supercell. After minimization, a NPT ensemble (a constant number of atoms, pressure and temperature) is used to increase the system temperature from 300 K to 600 K by a constant rate of 50 K/ns, and then a 12 ns NPT run at 600 K is used to generate PVDF melt with fully relaxed amorphous structure. To ensure the amorphous structures obtained are well equilibrated, the average radius of gyration ($R_g$), a quantity to describe the stretch degree of polymer chains, is monitored. As shown in Figure S1, $R_g$ gradually increases with the temperature from 300 K to 600 K, which corresponds to the increasing stretch degree of polymer chains. Finally, the oscillating convergence after 11 ns indicates the stable chain morphology, namely the equilibrium amorphous structure. The obtained structure is then quenched to different target temperatures, and NPT ensemble runs for 1 ns are used to further equilibrate the structures at the quenched temperatures. After the stable structures are obtained, the NVE ensemble (constant number of atoms, constant volume, and constant energy) runs for 2 ns are used to record heat flux and calculate thermal conductivity. Due to the isotropic structure of A-PVDF, thermal conductivity along all three directions are used to obtain an average value.

![Figure S1. Average radius of gyration from 40 polymer chains during heat treatment when equilibrate the amorphous PVDF structure.](image)
S3. Thermal conductivity and phonon density of states (PDOS) of A-PVDF.

Figure S2. (a) Thermal conductivity of A-PVDF versus temperature. (b) PDOS of A-PVDF along three directions at 300 K, 400K and 500 K.

S4. Size dependence of \( \kappa \).

Figure S3. Size dependence of thermal conductivity of PA-PVDF in (a) \( x \); (b) \( y \) and (c) \( z \) directions.

When using Green-Kubo formula to calculate thermal conductivity of PVDF array, the finite size effect would arise if the simulation cell is not large enough. Before studying the thermal conductivity, the simulation cell size is checked. We calculate the dependence of thermal conductivity of PA-PVDF
along all directions at 300 K. \( L_y \) and \( L_z \) are fixed as 1.9 nm and 2.5 nm when calculating \( \kappa_x \), respectively. \( L_x \) and \( L_z \) are fixed as 2.64 nm and 2.5 nm when calculating \( \kappa_y \), respectively. \( L_x \) and \( L_y \) are fixed as 2.37 nm and 1.9 nm when calculating \( \kappa_z \), respectively. As shown in Figure S2, \( \kappa_x \), \( \kappa_y \) and \( \kappa_z \) reach convergence when \( L_x \), \( L_y \) and \( L_z \) reach 2.64 nm, 2.37 nm and 5 nm, respectively. Therefore, 2.64 nm, 2.37 nm and 5 nm are chosen for \( L_x \), \( L_y \) and \( L_z \), respectively.

**S5. Integral of heat flux auto-correlation function (HCACF) of UA-PVDF and PA-PVDF.**

![Figure S4](image)

*Figure S4.* Integral of heat flux auto-correlation function (HCACF) in (a) \( x \); (b) \( y \); (c) \( z \) directions of UA-PVDF and PA-PVDF.

**S6. RDF and MSD of C and F atoms.**

The inter-chain RDF considers the separations of carbon atoms that are not in the same chain. The reference atom \((x_0, y_0, z_0)\) is the average coordinates of carbon atoms in a single chain. The distance from a reference carbon atom to atoms in other chains is defined as \( R = [(x-x_0) + (y-y_0)^2]^{1/2} \), with the pairs satisfying the criterion of \( |z-z_0| \leq 2 \) Å. This criterion is imposed to reduce noise in the RDF. Then, inter-chain RDF is calculated using \( g(r) = n/(2\pi r) \), where \( n \) is the number of carbon atoms with a distance of \( r < R < r + dr \) to the reference atom, and \( dr \) is set to be 0.1 Å. Like the three-dimensional RDF, inter-chain RDF reflects the atom density as a function of distance to a reference particle.
To understand the underlying mechanism of the different thermal conductivities between UAPVDF and PAPVDF, phonon density of state (PDOS) in three directions of them at different temperatures is calculated. The PDOS spectra are obtained through Fourier transform of velocity. PDOS in the full-frequency range is given in Figure S7, and an enlarged PDOS in the frequency range below 10 THz is presented in Figure S8. In $x$ and $y$ directions, low-frequency modes in PAPVDF shift to higher frequency region at 300K. For example, there is a sharp peak at about 1.1 THz in PDOS in $y$ direction of UAPVDF at 300K. When the structure is poled, this peak shows a clear blue-shift to higher frequency about 1.5 THz, which indicates hardening effect and higher group velocity of these phonon
modes [1]. Moreover, UAPVDF would induce more phonon scattering. As seen in Figure 5(b), there is an obvious peak at about 2.4 THZ in PDOS in y direction of PAPVDF at 300K. For UAPVDF, however, this peak merges with the peak at lower frequency and almost disappears, which indicates enhanced anharmonic phonon scattering and reduced phonon lifetimes [2]. Based on $\kappa = cv^2\tau/3$, the higher thermal conductivities in x and y directions of PAPVDF is attributed to higher phonon group velocities and longer phonon lifetimes along these two directions. Furthermore, results of PDOS indicate that two effects induced by structure poling mentioned above in y direction are stronger than that in x direction, and the least obvious in z direction. Thus, the enhancement ratio is biggest in y direction and least in z direction.

When temperature rises to 500K, PDOS in all three directions of PA-PVDF shift to low frequency regions, indicating reducing phonon group velocities. And pick width of PDOS is broaden, which means enhanced phonon-phonon scattering induced by increasing temperature. Thus, thermal conductivities of PA-PVDF decrease at higher temperature. Moreover, shape of PDOS of PA-PVDF at 500K is closer with that of UA-PVDF, which can explain the small distinction in thermal conductivities of two structures at high temperature. For UA-PVDF, differences between PDOS at 300K and 500K in x are sufficiently small, resulting similar thermal conductivities at these two temperatures. In y direction, pick around 1.1 THz is sharper at 500 K, but followed by many more flattened picks at higher frequencies. Eventually, these two kinds of changes cancel each other, resulting similar inter-chain thermal conductivity at different temperatures. Nevertheless, in z direction, most picks at 500K are more flattened than that at 300K in UA-PVDF, indicating more phonon scattering and lower $\kappa_z$ at higher temperature.
Figure S7. Phonon vibrational density of states in x, y and z direction in full-frequency range.
Figure S8. Phonon vibrational density of states in x, y and z direction below 10 THz.
S8. Spectral energy density in full-frequency range at 300 K.

Figure S9. SED maps of PA-PVDF along (a) Γ - X, (b) Γ - Y and (c) Γ - Z at 300K; and of UA-PVDF along (d) Γ - X, (e) Γ - Y and (f) Γ - Z in full-frequency range at 300K.
S9. Spectral energy density at 500 K.

Figure S10. SED maps of PA-PVDF along (a) \( \Gamma - X \), (b) \( \Gamma - Y \) and (c) \( \Gamma - Z \) at 300K; and of UA-PVDF along (d) \( \Gamma - X \), (e) \( \Gamma - Y \) and (f) \( \Gamma - Z \) in full-frequency range at 500K.
Figure S11. SED maps of PA-PVDF along (a) $\Gamma - X$, (b) $\Gamma - Y$ and (c) $\Gamma - Z$ at 300K; and of UA-PVDF along (d) $\Gamma - X$, (e) $\Gamma - Y$ and (f) $\Gamma - Z$ below 10 THz at 500K.
Reference

[1] X. Meng, T. Pandey, J. Jeong et al., Phys Rev Lett 122, 155901 (2019).

[2] X. Yu, R. Li, T. Shiga et al., J. Phys. Chem. C 123, 26735-26741 (2019).