

Electronic Supplementary Information

Monte Carlo simulations on temperature-dependent microstructure evolution of relaxor ferroelectric polymers

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S1. P(VDF-TrFE) relaxor ferroelectric based on asymmetric force field

In order to reveal the microstructure evolution of P(VDF-TrFE) relaxor ferroelectric during its phase transition, the distributions of orientation angle differences ($\Delta\theta$) between two nearest monomers and domain sizes (rs) within the bulk were estimated at different Monte Carlo (MC) simulation temperatures.

Distribution of orientation angle difference. As shown in [Fig. S1a](#), two peaks located at about 0° and 120° can be found in the probability distribution of orientation angle difference along the X direction at a certain temperature. At low temperature, most of unit dipoles (i.e., VDF-TrFE monomers) in P(VDF-TrFE) bulk are aligned in the same direction along the polymer chain direction, contributing to the highest peak at 0° . As the temperature increases, this 0° peak greatly reduces, and the 120° peak starts to emerge at around 900 K, indicating that most of unit dipoles are disorderly aligned along the X direction. Hence, the thermal energy may cause the reorientation of P(VDF-TrFE) polymer chains. As shown in [Fig. S1b](#), two peaks located at 0° and 120° can be found in the $\Delta\theta_Y$ probability distribution at 100 K. In addition, the tiny 0° peak can be ignored, since it disappears soon as the temperature increases, while the large 120° peak can maintain until the temperature rises to 900 K. This 120° peak indicates the alternating alignment between unit dipoles along the Y direction. As shown in [Fig. S1c](#), the $\Delta\theta_Z$ probability distribution exhibits a more complicated situation, different from the $\Delta\theta_X/\Delta\theta_Y$ probability distributions. At the initial 100 K, five peaks locate at 0° , 30° , 60° , 90° , and 120° respectively. Once the temperature rises, the 60° peak disappears. Then, the 0° and 120° peaks disappeared at 300 K and merges into the 30° and 90° peaks to form new wide peaks. At 600 K, the 30° peak further merges into the 90° peak. The left 90° peak finally vanishes above 900 K.

These characteristic orientation angle difference probability distribution between two neighboring unit dipoles surely corresponds to the first phase transition at 300 K and the second phase transition at 900 K of P(VDF-TrFE) relaxor ferroelectric. The studied system becomes more and more disordered as the temperature increases. Above 900 K, all the

distributions of the orientation angle differences along three directions have been equalized.

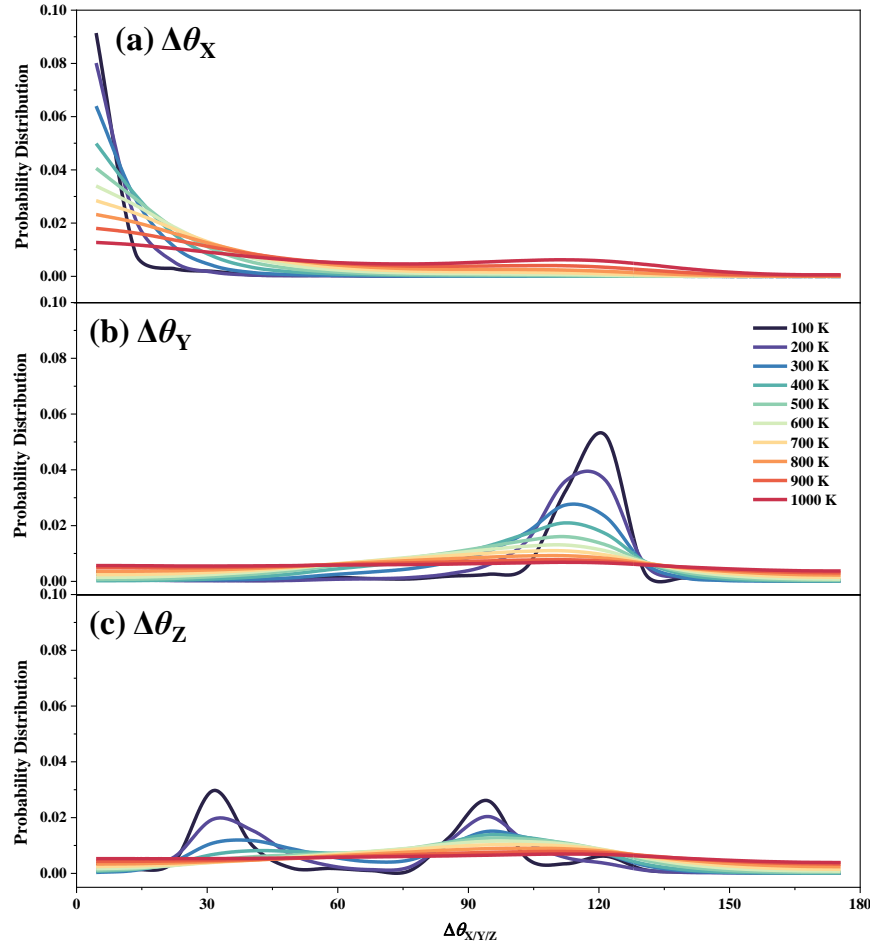


Fig. S1 Distributions of orientation angle differences along (a) X, (b) Y, and (c) Z directions of P(VDF-TrFE) relaxor ferroelectric in the temperature range of 100-1000 K derived from MC simulations based on the asymmetric force field.

Domain evolution. The volume fractions for different types of nanostructures in [Fig. 3](#) of the **main text** were estimated according to the analysis on the probability distribution of domain size of P(VDF-TrFE) relaxor ferroelectric under varied temperatures here in [Fig. S2](#). The r probability distribution has been divided into four small figures according to varied domain size ranges or different temperature ranges.

As shown in **Fig. S2a**, the microstructure evolution information about single dipoles and microdomains is present here. Since the size of single dipole, VDF-TrFE monomer, is about 0.5 nm, the r distribution densely populates at about 0.2 nm, corresponding to a great number of single dipoles within P(VDF-TrFE) bulk. They greatly exist even when the temperature is as high as 1000 K. Upon the rise of temperature, these disperse single dipoles decrease, and the domain size distributes between 0.5 nm and 2.0 nm, indicating the appearance of microdomains. Especially at 300 K, the r distribution has three peaks located at 1.25 nm, 1.65 nm, and 1.85 nm, signifying considerable growth of microdomains for the first phase transition. These peaks disappear soon at 400 K, ensuring this phase transition. As shown in **Fig. S2b**, the r distribution spans over the 3.5-7 nm below 600 K. This size corresponds to nanodomains. At 100 K, the dominating r distribution is naturally divided into two intervals with an explicit boundary at around 4.75 nm. This value is employed to distinguish between nanodomains and large nanodomains. At 100 K, nanodomains and large nanodomains exist in large quantities within the P(VDF-TrFE) bulk. With the increase in temperature, both nanodomains and large nanodomains decrease a lot, and the large nanodomains reduce faster. However, the higher and narrower peak appears at about 3.9 nm in the r distribution, indicating that nanodomains dominate in the bulk. In the temperature range of 400-600 K, the multiple small peaks emerge, corresponding to the slush model¹ for domain evolution in P(VDF-TrFE) bulk. They gradually disappear above 600 K. When the temperature is higher than 600 K, the domain size starts to distribute at the region larger than 7 nm, corresponding to the emergence of large nanodomain with randomly oriented dipoles (RLNDs). As shown in **Fig. S2c**, the r distribution more and more densely populates around 8-10.5 nm as the temperature further increases above 600 K. Beyond our chemical intuition, these RLNDs have a long life even at high temperature, as indicated by the dense distribution around 8.5-10.5 nm in the temperature range of 1100-2000 K in **Fig. S2d**. These RLNDs can be regarded as the precursor of paraelectric phase. At the next stage, the P(VDF-TrFE) relaxor ferroelectric would undergoes the paraelectric

phase driven by thermal energy.

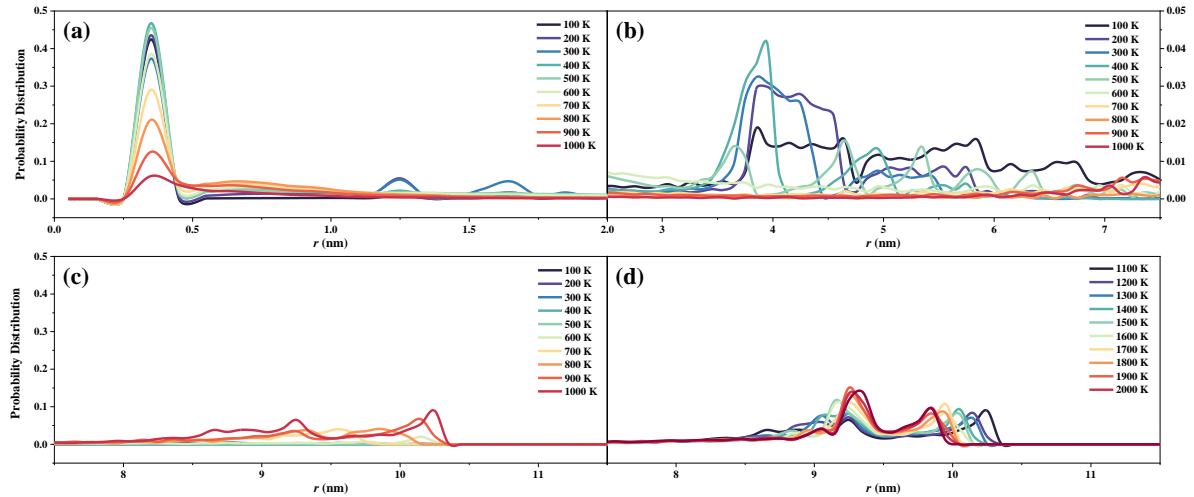


Fig. S2 Distributions of domain sizes (a-d) of P(VDF-TrFE) relaxor ferroelectric in the temperature range of 100-2000 K derived from MC simulations based on the asymmetric force field.

Analysis of size effect based on domain volume fraction comparison. After a series of MC simulations on the large-size P(VDF-TrFE) relaxor ferroelectric with its volume of $49.3 \text{ nm} \times 59.8 \text{ nm} \times 59.6 \text{ nm}$ ($100 \times 100 \times 100$ supercell) at different temperatures (100-1200 K), its microstructure evolution was also estimated in [Fig. S3](#) to compare with that of the small-size P(VDF-TrFE) relaxor ferroelectric, whose volume is as large as $24.8 \text{ nm} \times 29.9 \text{ nm} \times 29.8 \text{ nm}$ ($50 \times 50 \times 50$ supercell), to discuss their size effect on temperature-dependent microstructure evolution. Noticeably, the volume fraction of microdomains (1.0-2.5 nm), nanodomains (2.5-5.0 nm), and large nanodomains (5.0-8.0 nm) are gathered together to estimate their total volume fraction for simple and clear comparison between simulated systems with various sizes. The size change of simulated systems does not affect sizes of observed nanoscale domains, but it causes the change in relative magnitudes of volume fractions of typical domains. Especially, the volume fraction (about 0.81) of LNDs + NDs + MicroDs largely increases in large-size P(VDF-TrFE) bulk when $T = 100 \text{ K}$

compared to that (0.43) in small-size bulk. When the large-size simulated system is adopted, the content of LNDs increases a lot at low temperature. This can be well understood that these high-content LNDs results from the contribution of low-temperature ferroelectric phase. Noticeably, the peak values and the temperature ranges at which these peaks appear, for single dipoles, RLNDs, and LNDs + NDs + MicroDs, have remained unchanged. This indicates the whole phase transition pictures for both systems remain identical.

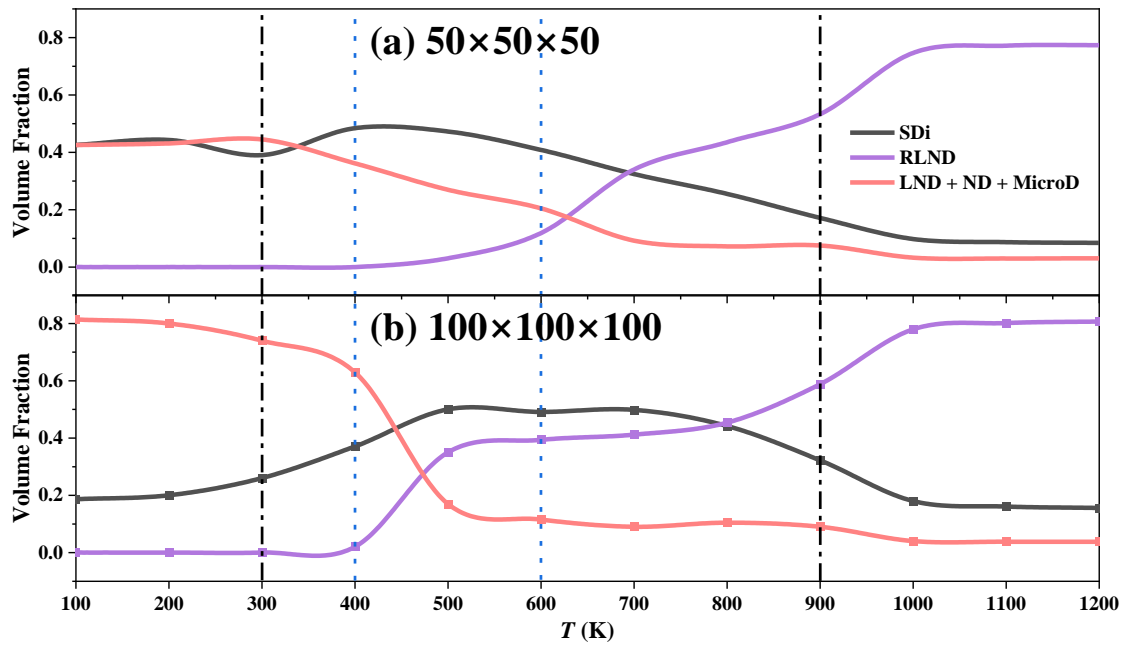


Fig. S3 Variations of volume fraction for SDi, RLND, or LND + ND + MicroD with temperature involved in P(VDF-TrFE) relaxor ferroelectric derived from MC simulations based on (a) $50 \times 50 \times 50$ and (b) $100 \times 100 \times 100$ supercells. SDi, MicroD, ND, LND, and RLND indicate single dipole, microdomain, nanodomain, large nanodomain, and large nanodomain with randomly oriented dipoles respectively.

Frequency-dependent dielectric spectra. As shown in [Fig. S4](#), the frequency-dependent dielectric spectra were further estimated to highlight the important signature of relaxor behaviors in dielectric response. As the AC frequency increases from 1 kHz to 1.78 kHz,

the wide dielectric peaks under different frequencies shifts toward higher temperatures and these peak values tend to become larger for P(VDF-TrFE) relaxor ferroelectrics. In contrast to P(VDF-TrFE) normal ferroelectrics, their dielectric peaks do not shift and their peak values tend to become smaller as the AC frequency increases, exhibiting frequency-independent dielectric anomaly.

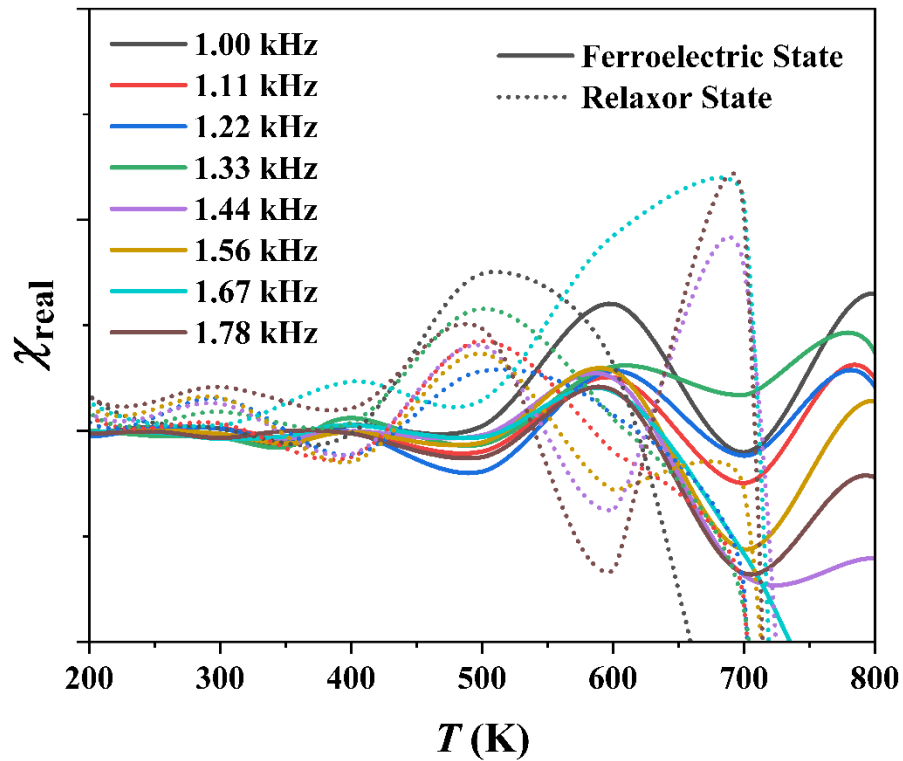


Fig. S4 Dielectric permittivity comparison between P(VDF-TrFE) ferroelectric and relaxor ferroelectric states derived from our MC simulations by using symmetric and asymmetric force fields respectively.

S2. P(VDF-TrFE) ferroelectric based on symmetric force field

Total energy, heat capacity, and polarizations. Different from the tendencies of total energy and heat capacity (see Fig. 2a) and polarizations (see Fig. 2b) of P(VDF-TrFE) relaxor ferroelectric in the **main text**, the P(VDF-TrFE) normal ferroelectric possesses its own characteristic $E-T$, C_V-T , and $P_Y/P_Z/P_{\text{tot}}-T$ curves here in Fig. S5. Because the system undergoes the ferroelectric-paraelectric phase transition, the total energy consistently increases with temperature in Fig. S5a. The C_V-T curve has a peak value at 300 K and a broadening tailing after 300 K. With the increase in temperature, the polarizations along the Y and Z directions with values of $8.47 \mu\text{C}/\text{cm}^2$ and $-8.62 \mu\text{C}/\text{cm}^2$ respectively decrease/increase to zero in Fig. S5b. The total polarization varies from $12.09 \mu\text{C}/\text{cm}^2$ to zero, completely lining with experimental values ($\pm 10 \mu\text{C}/\text{cm}^2$) of P(VDF-TrFE) (50/50 mol %) ferroelectrics.² Noticeably, the polarizations become zero when temperature approaches to 2000 K, proving again that the MC simulation temperatures do not match the real temperatures. All of these results strongly support that our developed symmetric force field excellently reproduces the ferroelectric-paraelectric phase transition of P(VDF-TrFE) ferroelectric.

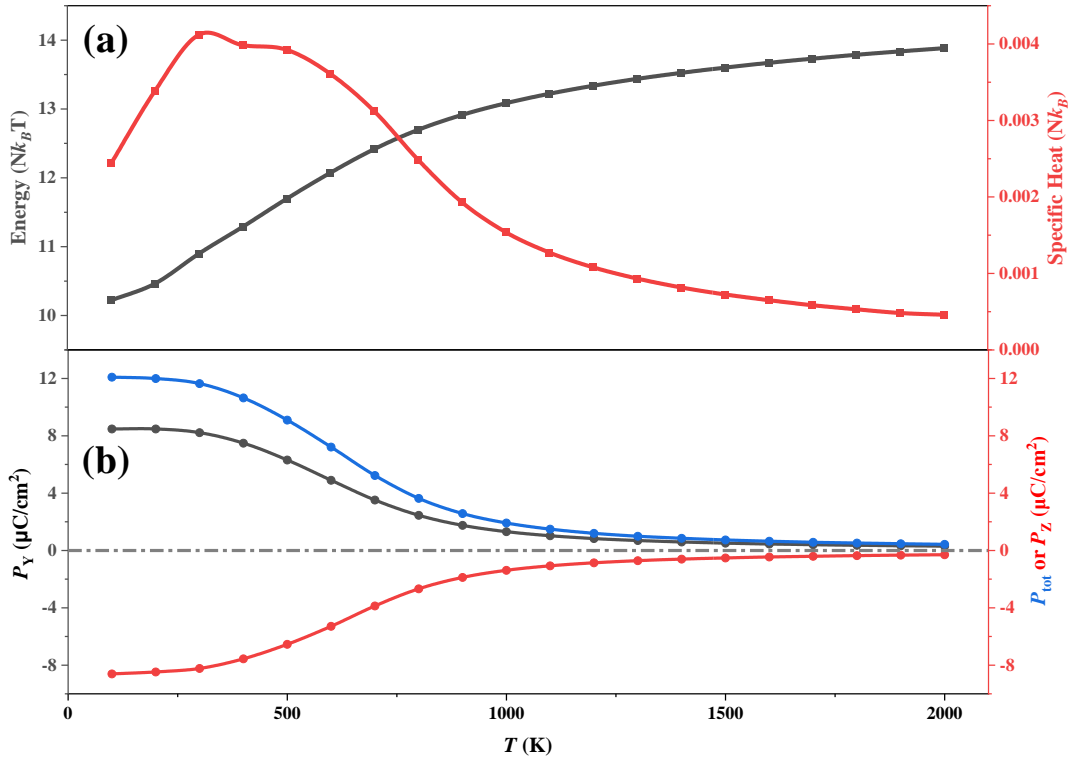


Fig. S5 Variations of (a) energy/heat capacity and (b) polarizations along Y (P_Y) and Z directions (P_Z) and total polarization (P_{tot}) of P(VDF-TrFE) ferroelectric with temperature in the range of 100-2000 K derived from MC simulations based on the symmetric force field.

Distribution of orientation angle difference. As shown in [Fig. S6a](#), the characteristic $\Delta\theta_X$ distribution between two neighboring unit dipoles in P(VDF-TrFE) ferroelectric is quite similar to that (see [Fig. S1a](#)) in P(VDF-TrFE) relaxor ferroelectric with two peaks located at 0° and 120° . The parallel dipoles tend to become more and more disordered upon the rise of temperature. As shown in [Fig. S6b and S6c](#), the P(VDF-TrFE) ferroelectric exhibits more orderly dipole orientations along both Y and Z directions, compared to the P(VDF-TrFE) relaxor ferroelectric [see [Fig. S1b and S1c](#)]. At 100 K, the $\Delta\theta_Y/\Delta\theta_Z$ probability distributions densely populate at 30° . Above 300 K, the 30° peak disappears, shifts to 0° , and become a wide peak. Above 900 K, the wide peak disappears. All of these results from

the thermal-energy-contributed ferroelectric-paraelectric phase transition.

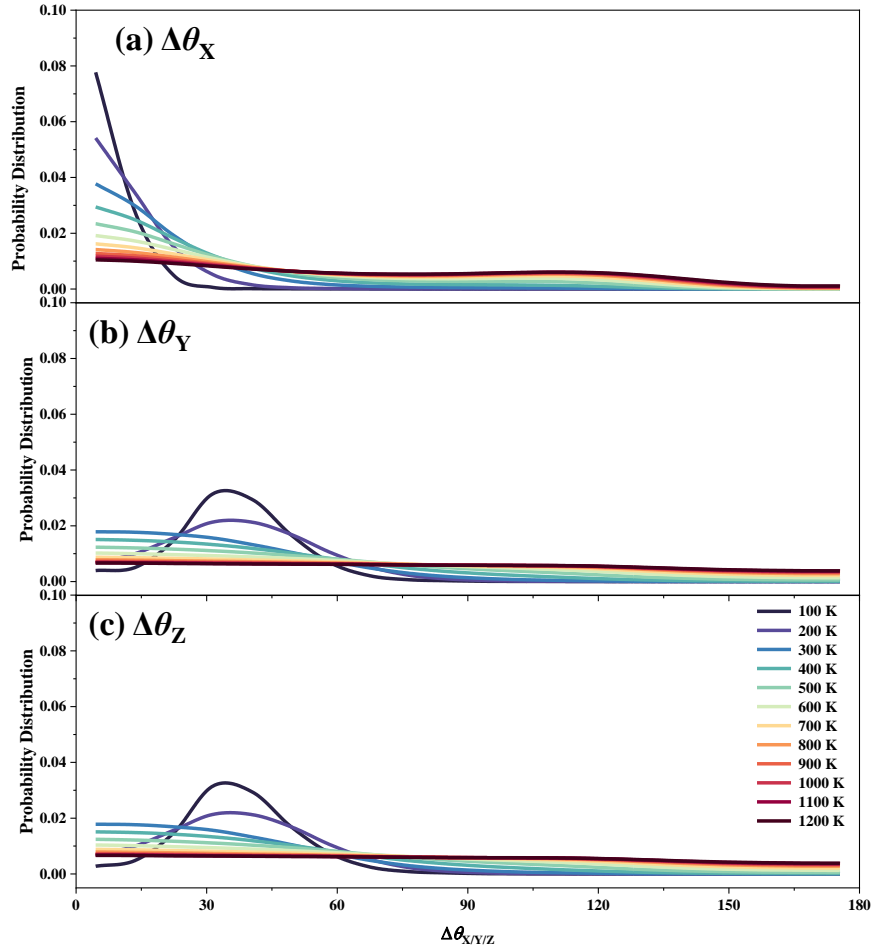


Fig. S6 Distributions of orientation angle differences along the (a) X, (b) Y, and (c) Z directions P(VDF-TrFE) ferroelectric in the temperature range of 100-1200 K derived from MC simulations based on the symmetric force field.

Domain evolution. As shown in [Fig. S7](#), the P(VDF-TrFE) ferroelectric exhibit the greatest difference for domain evolution, compared to that of the P(VDF-TrFE) relaxor ferroelectric (see [Fig. S2](#)). The domain size distributions at varied temperatures here have two-peaks feature. These two peaks locate in the range of 0-2.5 nm and 6-13.2 nm respectively. Different from the relaxor system, the normal ferroelectric here only contains

single dipoles and ferroelectric domains, no microdomains and nanodomains found in relaxor ferroelectric. At 100 K, the large 13.2-nm peak corresponds to the ferroelectric domains, and the small 0.5-nm peak corresponds to single domains, indicating the existence of a small amount of disperse single dipoles in the bulk. As the temperature increases, the ferroelectric domains largely reduce and their size decreases at the same time, while the single dipoles greatly increase. The ferroelectric domains eventually vanished at around 1000 K, indicating formation of the paraelectric phase.

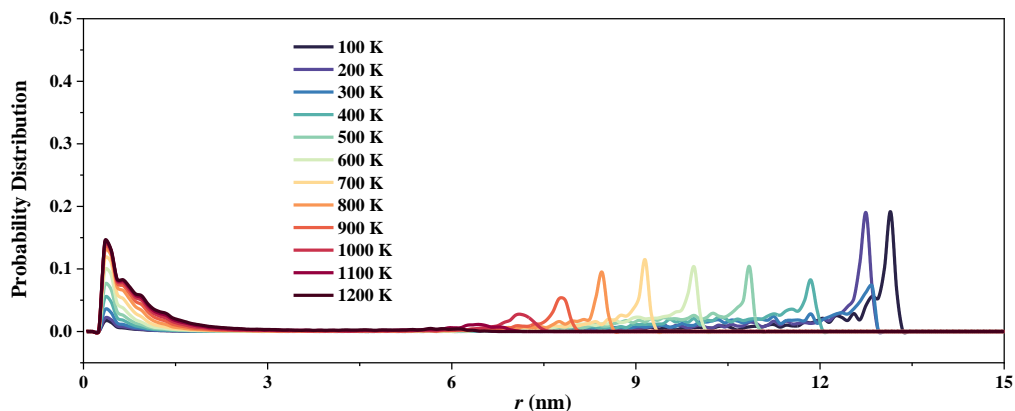


Fig. S7 Distributions of domain sizes of P(VDF-TrFE) ferroelectric in the temperature range of 100-1200 K derived from MC simulations based on the symmetric force field.

Variation of free energy with temperature. As shown in [Fig. S8](#), the Gibbs free change as a function of domain size of P(VDF-TrFE) normal ferroelectric at a certain temperature exhibits one-peak feature, different from temperature-dependent multiple-peaks (at low temperatures) or single-peak features (at high temperatures) of P(VDF-TrFE) relaxor ferroelectric in [Fig. 4](#). The peak values correspond to the critical nucleation sizes of P(VDF-TrFE) ferroelectric at varied temperatures, locating at 4-5 nm. Although this domain size is comparable to the size of nanodomains in P(VDF-TrFE) relaxor ferroelectric, these nucleated domains are growing into ferroelectric domains. With the increase in temperature, the critical nucleation size reduces, changing from 5 nm to 4 nm, but the

nucleation energy barrier increases a lot. Surely, the ferroelectric system is difficult to form ferroelectric domains at high temperatures. Noticeably, each nucleation energy barrier at a certain temperature of P(VDF-TrFE) ferroelectric is much lower than that of P(VDF-TrFE) relaxor ferroelectric.

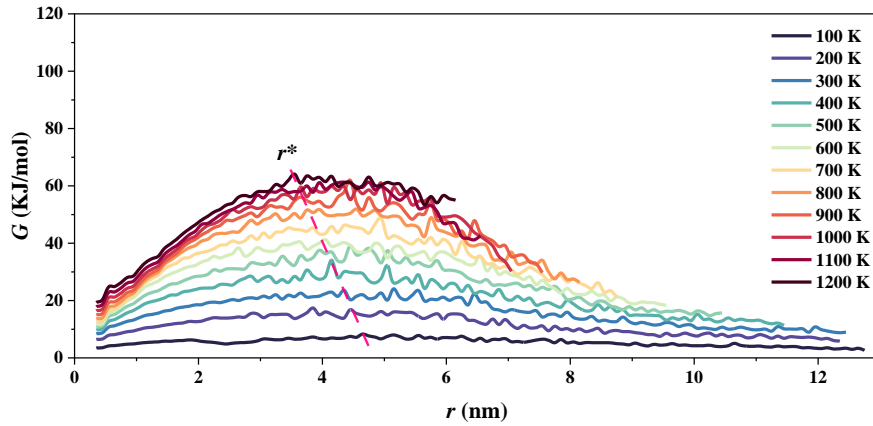


Fig. S8 Variation of free energy with domain size of P(VDF-TrFE) ferroelectric under different temperatures from 100 K to 1200 K derived from MC simulations based on the symmetric force field.

Supplementary references

1 H. Takenaka, I. Grinberg, S. Liu and A. M. Rappe, *Nature*, 2017, **546**, 391-395.

2 Q. M. Zhang, V. V. Bharti and X. Zhao, *Science*, 1998, **280**, 2101-2104.