Supporting Information

Modulating thermal conductivity of crystalline nylon by tuning hydrogen bonding through structure poling

Shichen Deng[1], Dengke Ma[2,*], Guangzu Zhang[3], Nuo Yang[1,*]

[1] State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, P. R. China

[2] NNU-SULI Thermal Energy Research Center (NSTER) & Center for Quantum Transport and Thermal Energy Science (CQTES), School of Physics and Technology, Nanjing Normal University, Nanjing, 210023, P. R. China

[3] School of Optical and Electronic Information and Wuhan National Laboratory of Optoelectronics, Huazhong University of Science and Technology (HUST), Wuhan, 430074, P. R. China

E-mail: D.M. (dengke@njnu.edu.cn) and N.Y. (nuo@hust.edu.cn)

S1. The EMD simulation details.

All EMD simulation details are given in Table S1. The 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, τ is the correlation time, τ_0 is the integral upper limit of heat current auto-correlation function (HCACF), E is the total kinetic energy of the group of atoms, N is the number of total atoms, and the angular bracket denotes an ensemble average.

Table S1. Detailed progress and parameter settings in molecular dynamics simulation.

Method	EMD (Green-Kubo method)				
Force field	PCFF				
Boundary conditions	$x\ y\ z$: p p p				
Simulation process					
Ensemble	**Settings**				**Purpose**
NPT	Time step (fs)	0.25	Runtime (ns)	0.1	Relax structure
	Temperature (K)	300	Pressure (atm)	1	
NVE	Time step (fs)	0.25	Runtime (ns)	0.1	Relax structure
	Temperature (K)	300			
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	$\kappa = \frac{V}{3 k_B T^2} \int_0^{\tau_0} \langle \vec{J}(0) \cdot \vec{J}(\tau) \rangle d\tau$				

h1   h2

-CONH-(CH2)n-

c1   c2

Atom type	Charge (e)	ε (kcal/mol)	σ (Å)
c1	0.642	0.120	4.01
c2	0.104	0.054	3.81
n	-0.699	0.106	3.60
o	-0.531	0.267	3.30
h1	0.053	0.013	1.65
h2	0.378	0.02	2.995

Scheme S1. Partial charges and LJ (12-6) potential parameters of all atom types.

S2. The convergence test in size dependence of κ.

When studying the thermal conductivity (κ), the dependence of κ on simulation cell size is checked. When the cell is too small, some phonons, whose wavelengths are longer than the cell size, cannot survive in the system. Hence, increasing the domain size will include more long-wavelength phonons in simulation, which contributes to thermal conductivity. When the simulation cell is large enough, the value of thermal conductivity converges due to a competing effect of increasing on both phonon modes and scattering.

The dependence of thermal conductivity of PN-5 along all directions at 300 K is calculated. (1) L_y and L_z are fixed as 2.4 nm and 1.8 nm, and L_x is increased from 2.2 to 7.3 nm. Then, κ_x is calculated and shown in Fig. S1(a). (2) L_x and L_z are fixed as 3.7 nm and 1.8 nm, and L_y is increased from 1.4 to 2.9 nm. Then, κ_y is calculated and shown in Fig. S1(b). (3) L_x and L_y are fixed as 3.7 nm and 1.9 nm, and L_z is increased from 0.7 to 2.2 nm. Then, κ_z is calculated and shown in Fig. S1(c).

As shown in Fig. S1, κ_x, κ_y and κ_z reach converged values when L_x, L_y and L_z are larger than 5.1 nm, 2.4 nm and 1.1 nm, respectively. Therefore, to obtain the size-independent values of thermal conductivity by EMD, 7.3 nm, 2.9 nm and 2.2 nm are chosen for L_x, L_y and L_z, respectively, in simulations reported in the main text.
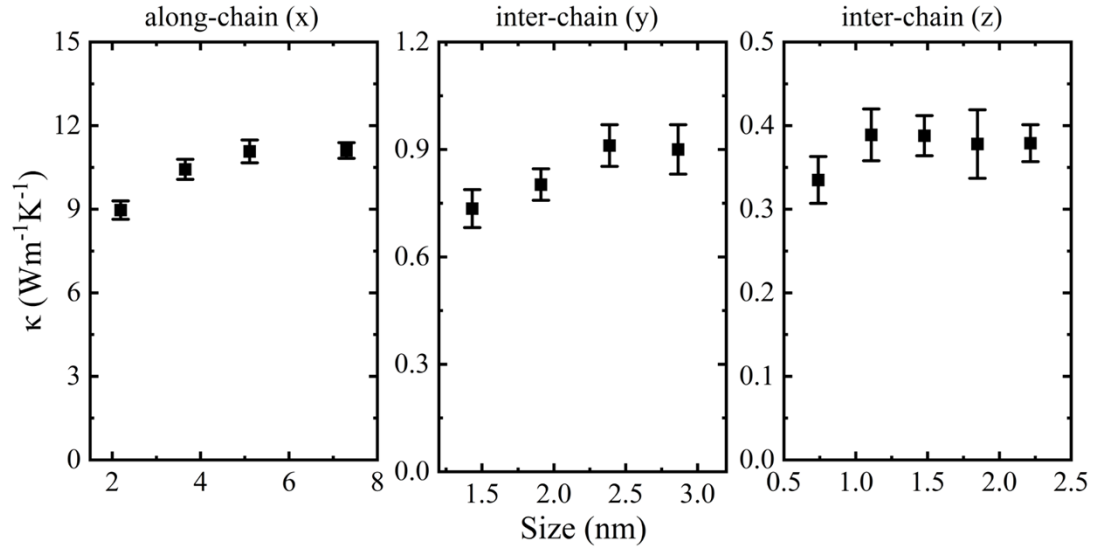
Fig. S1. Convergence test in size dependence of thermal conductivity of PA-PVDF in (a) *x*; (b) *y* and (c) z directions.

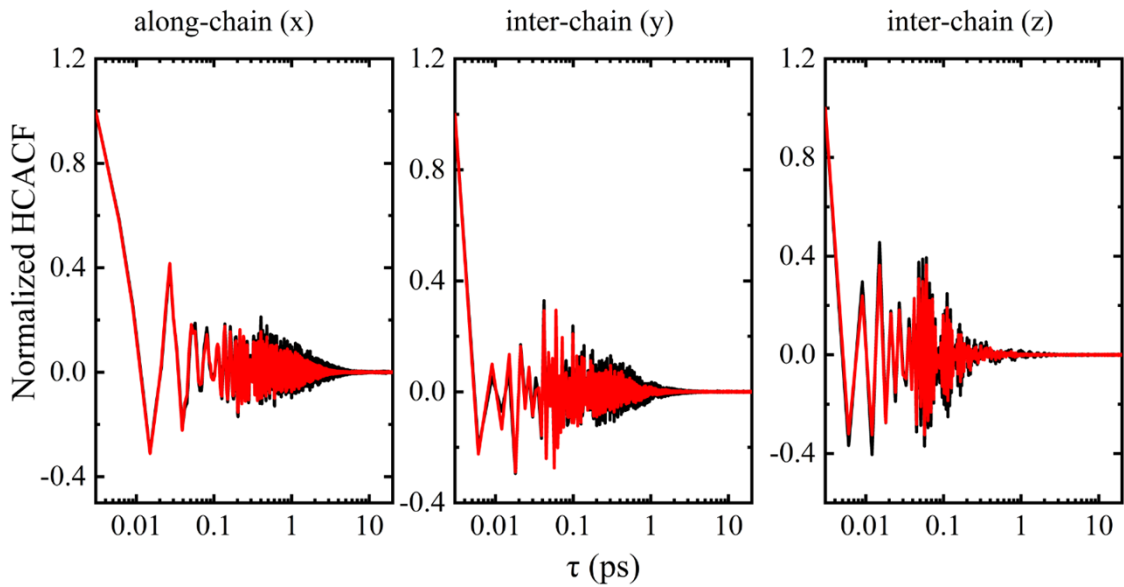## S3. Integral of heat flux auto-correlation function (HCACF) of UN-5 and PN-5.

Fig. S2. Heat flux auto-correlation function (HCACF) in (a) x; (b) y; (c) z directions of UN-5 and PN-5.
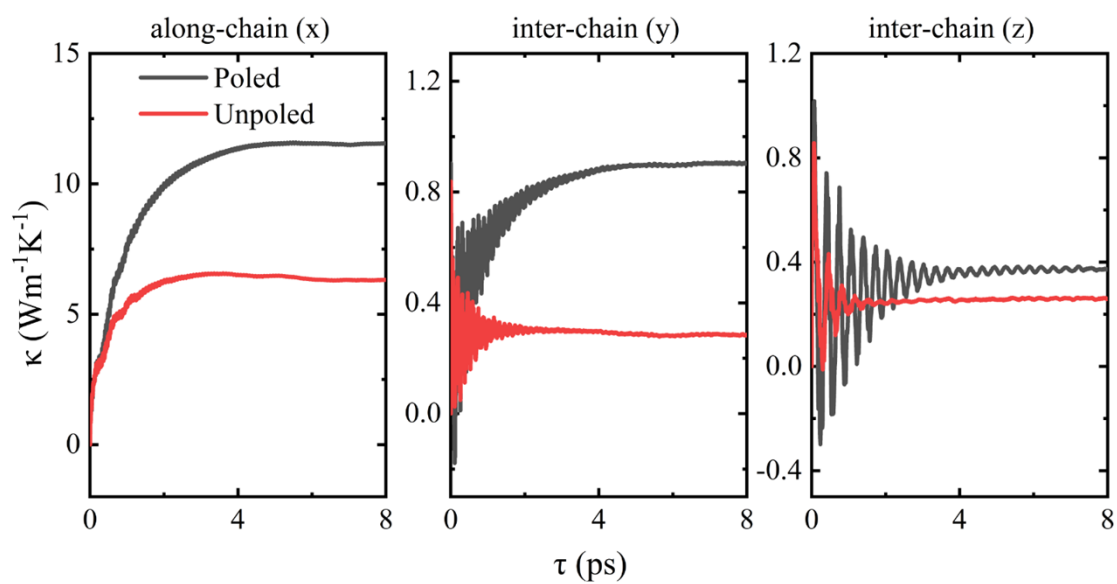
Fig. S3. Integral of heat flux auto-correlation function (HCACF) in (a) *x*; (b) *y*; (c) z directions of UN-5 and PN-5.

S4. Structure plots in xz plane after relaxation of unpoled and poled nylons.
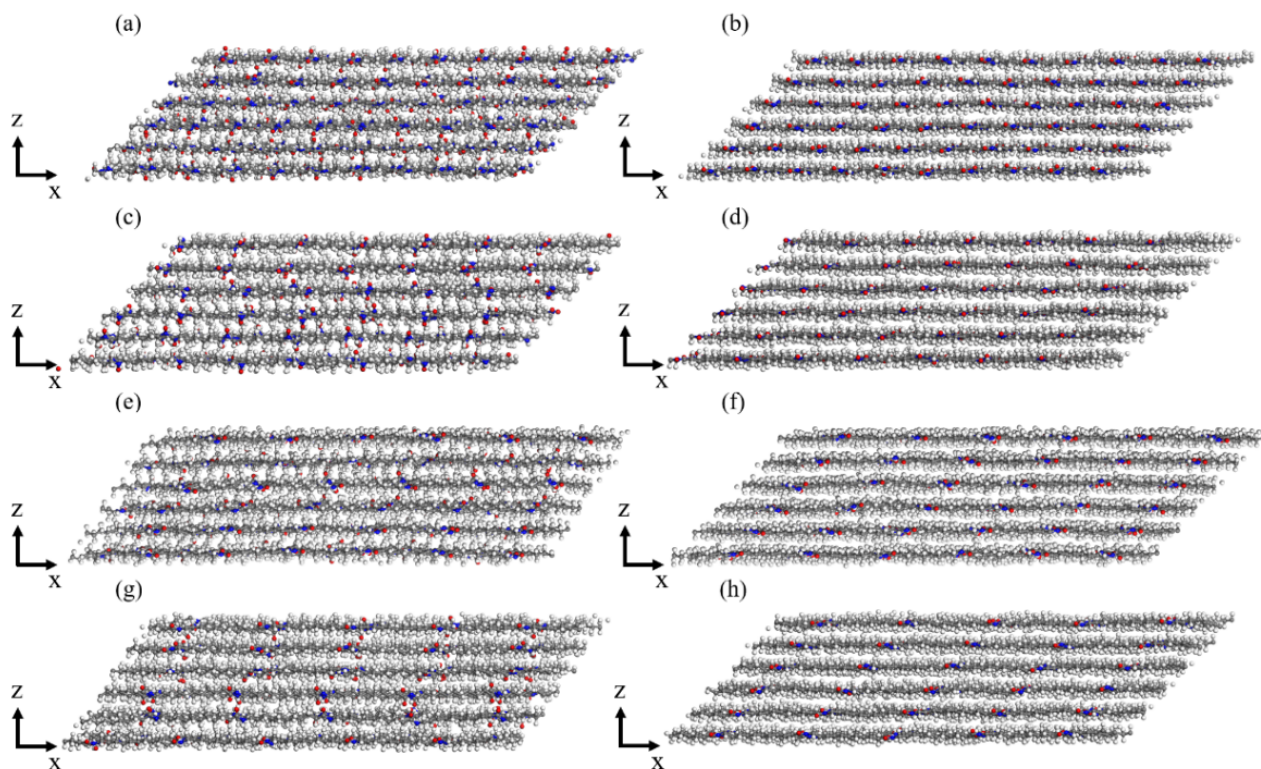
Fig. S4. Figure S4. Structure plots in xz plane after relaxation of (a) UN-5; (b) PN-5; (c) UN-7; (d) PN-7; (e) UN-9; (f) PN-9; (g) UN-11; (h) PN-11.
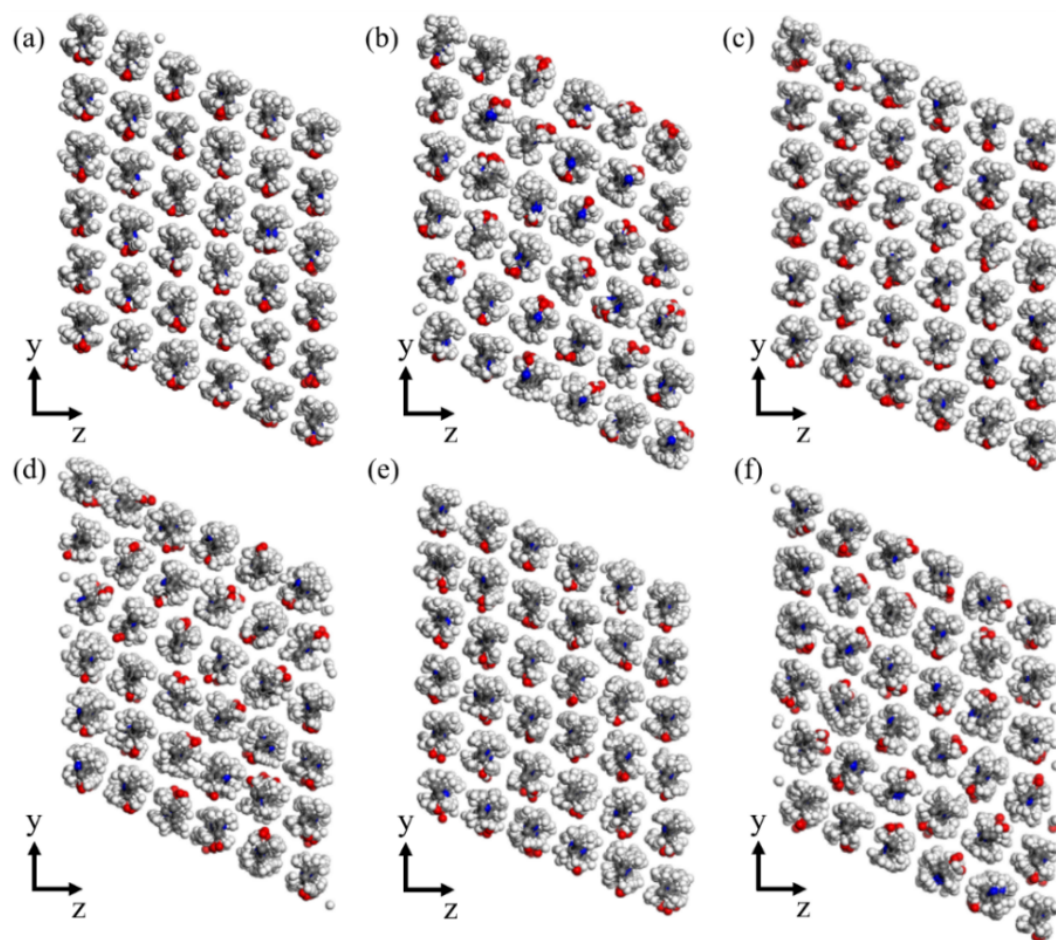
S5. Relaxed structure of other nylons.

Fig. S5. Structures after relaxation of (a) PN-7; (b) UN-7; (c) PN-9; (d) UN-9; (e) PN-11; (f) UN-11.

S6. Details of hydrogen bonds calculation.

The coordinates of the N, H and O atoms in amide groups are recorded at each step. The distance between an O atom in an amide group and an H atom in the nearest amide group, and the angle formed by an O atom in an amide group and N, H atoms in the nearest amide group, are calculated. If the distance is shorter than 0.35 nm and the angel is larger than 145°, the hydrogen bond is assumed to be formed between the two amide groups. Densities of hydrogen bonds in the unpoled and poled structures of different nylons versus the simulation time are shown in Fig. S6.
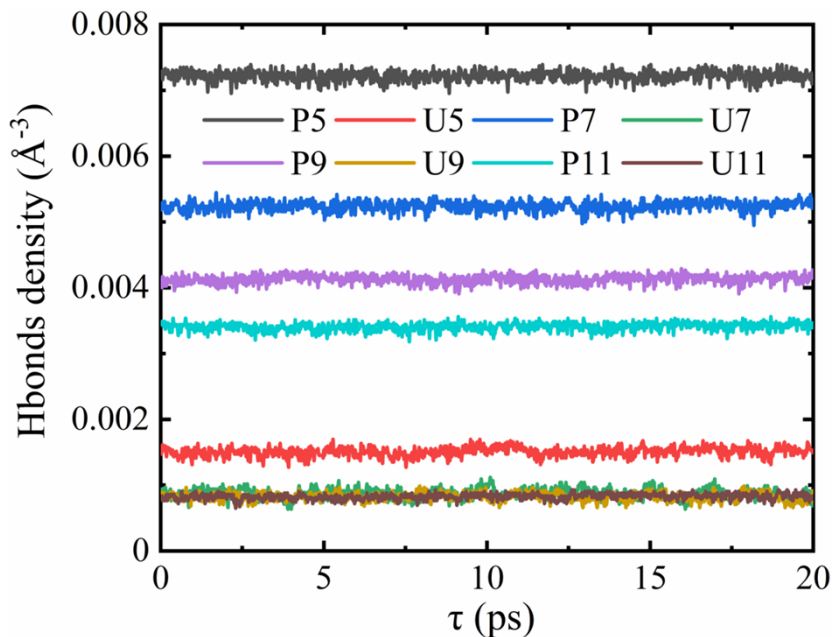
Fig. S6. Densities of hydrogen bonds in unpoled and poled structures of different nylons versus the simulation time.

S7. RDF calculation details and RDF of other nylons.

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 $R = [(z-z_0) + (y-y_0)^2]^{1/2}$, with the pairs satisfying the criterion of $|x-x_0| \leq 3$ 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 ($r < R < r + dr$) 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.

The along-chain RDF is one-dimensional, characterizing the lattice order within one chain. Taking one carbon atom (x_0, y_0, z_0) as the reference atom, its distance to other carbon atoms in the x-direction within the same chain is defined as $R = |x - x_0|$. Then, the along-chain RDF is recorded as $g(r) = n$, where n is the number of carbon atoms with a distance of R ($r < R < r + dr$) to the reference atom.
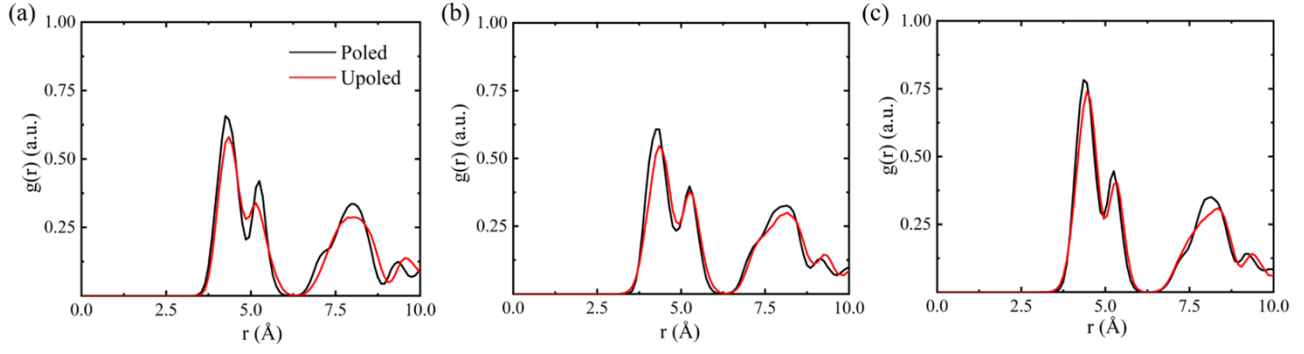
Fig. S7. Inter-chain radial distribution function (a) UN-7 and PN-7; (b) UN-9 and PN-9; (e) UN-11 and PN-11.
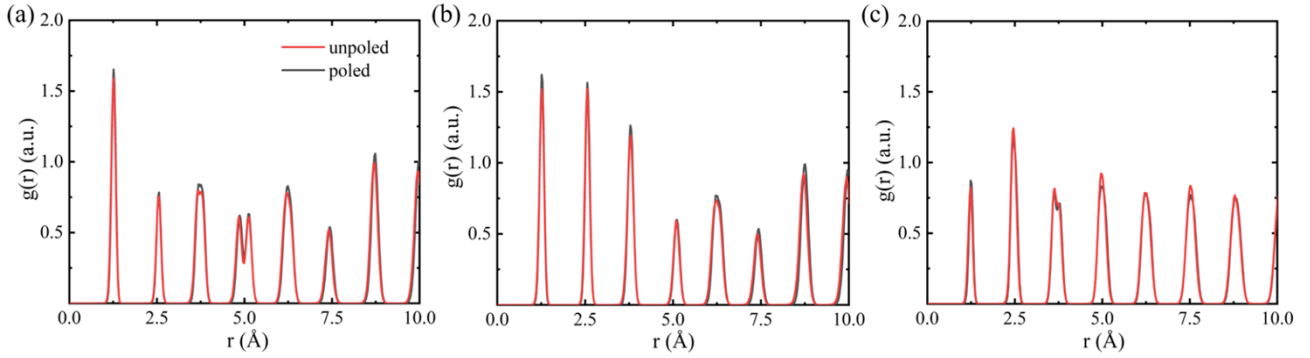

Fig. S8. Along-chain radial distribution function (a) UN-7 and PN-7; (b) UN-9 and PN-9; (e) UN-11 and PN-11.
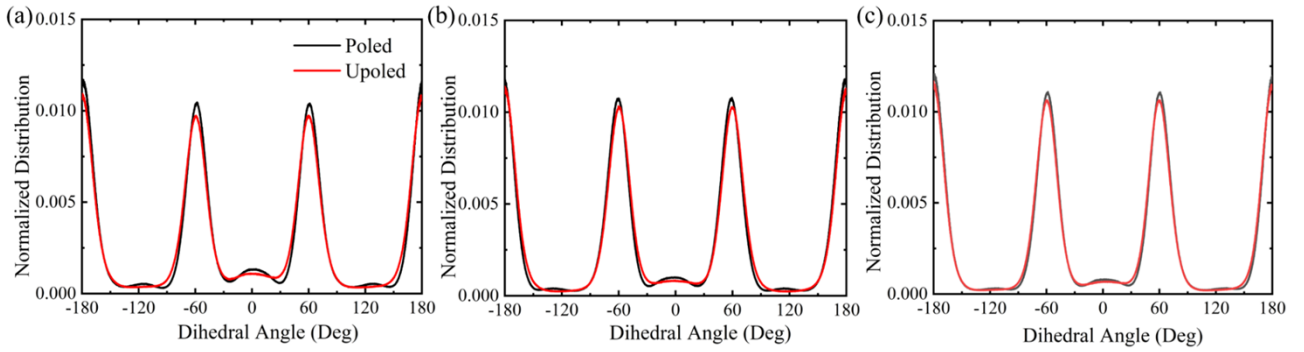
S8. Distribution of dihedral of other nylons.

Fig. S9. Distribution of dihedrals of (a) UN-7 and PN-7; (b) UN-9 and PN-9; (c) UN-11 and PN-11.

S9. Phonon density of states in the full frequency range.

The vibrational density of states (vDOS) is calculated based on Parseval's theorem, the mass-weighted power spectra $P(\omega)$ are calculated based on velocities. Then vDOS is expressed as

$$P(\omega) = \frac{1}{N}\sum_{i=1}^{N} m_i |\frac{1}{\sqrt{2\pi}}\int v_i(t)e^{-i\omega t}dt|^2$$

, here ω is the angular frequency, N is the number of atoms, m is the atomic mass, v is the velocity, and t is the time interval. We recorded the trajectory of nylons for 1 nanosecond, then performed fast a Fourier transform and multiple time average to obtain the power spectra. vDOS in the full-frequency range is given in Fig. S10.
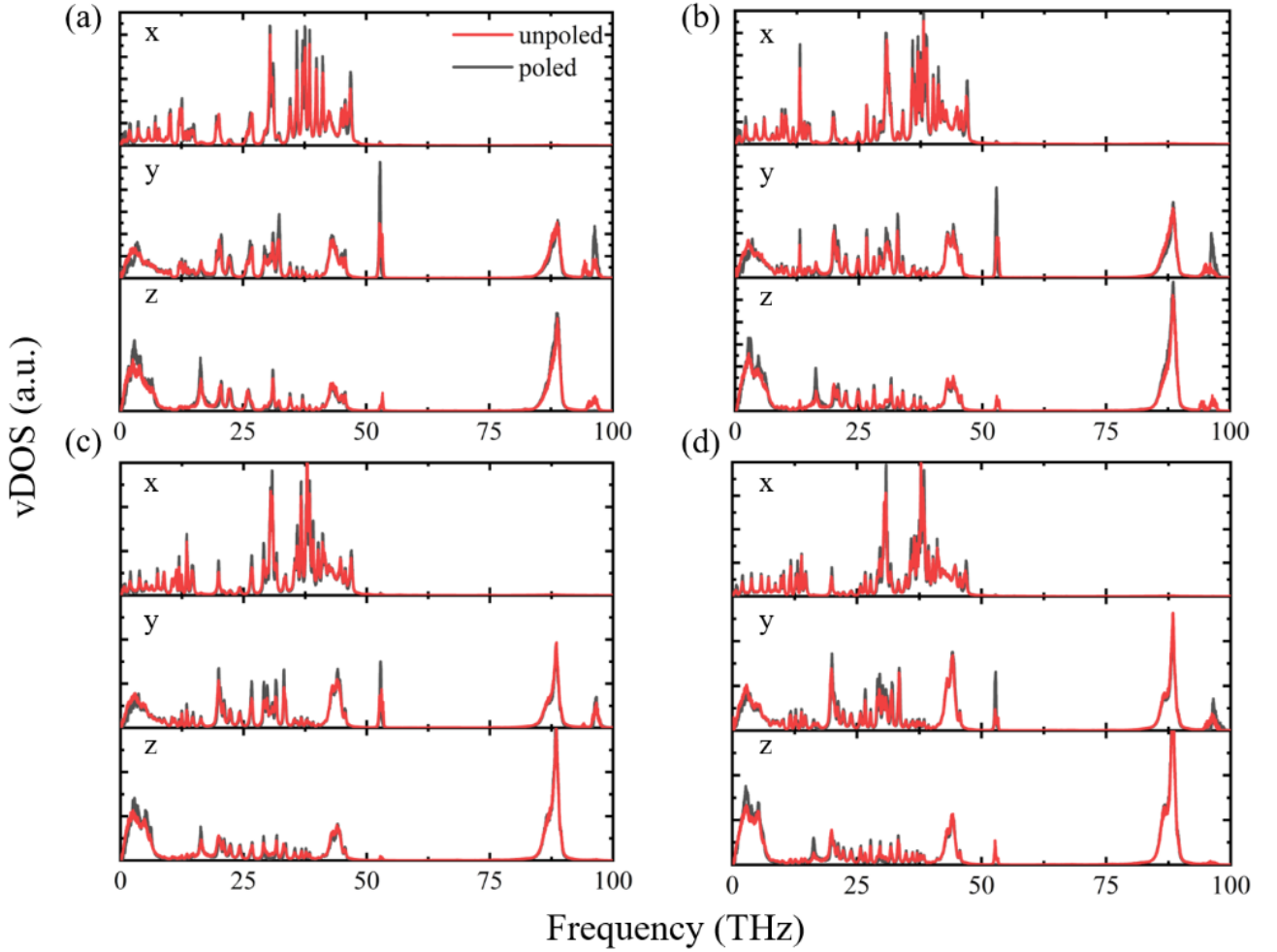

Fig. S10. vDOS comparation between unpoled and poled structures of (a) nylon5; (b) nylon7; (c) nylon9 and (d) nylon11 in full frequency range.

S10. Structure of UN-5 after relaxing in different electric fields along the y-direction.
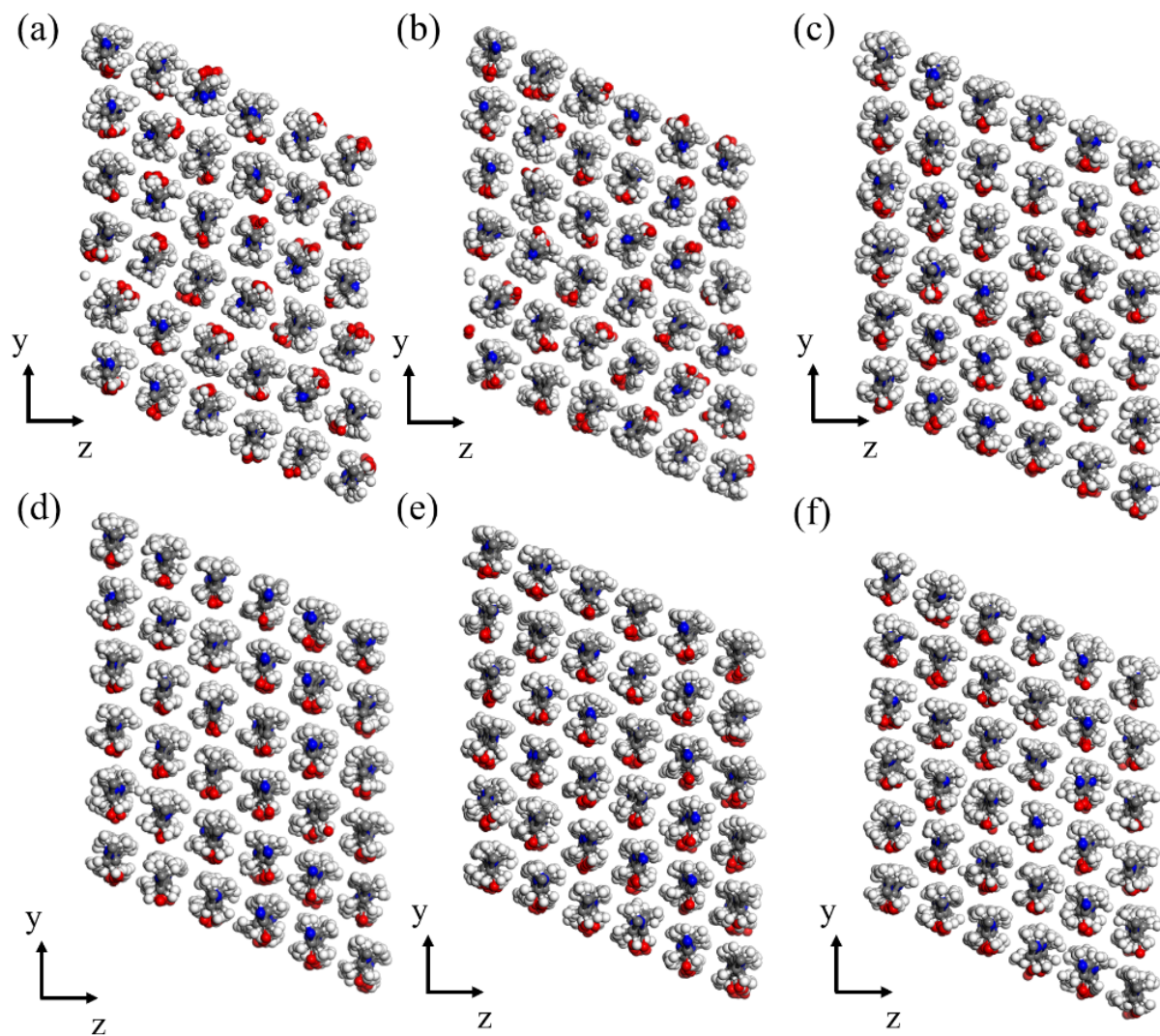

Fig. S11. Structure of UN-5 after relaxing in electric field along y direction with intensities of (a) 1.0; (b) 1.5; (c) 2.0; (d) 2.5; (e) 3.0; (f) 3.5 V/nm.