

Electronic Supplementary Information (ESI)

## Tuning Thermal Conductivity of Crystalline Polymer Nanofibers by Interchain Hydrogen Bonding

Lin Zhang,<sup>a</sup> Morgan Ruesch,<sup>a</sup> Xiaoliang Zhang,<sup>b</sup> Zhitong Bai,<sup>a</sup> and Ling Liu<sup>a1</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering, Utah State University, Logan, UT 84322, USA

<sup>b</sup> Institute of Mineral Engineering, Division of Materials Science and Engineering, Faculty of Georesources and Materials Engineering, Rheinisch-Westfaelische Technische Hochschule (RWTH Aachen University), 52064 Aachen, Germany.

**1. OPLSAA force field:** We used OPLSAA force field<sup>1,2</sup> to describe interatomic interactions for nylon nanocrystals. The total potential energy comprises non-bonded potential, bond stretching potential, angle bending potential, and torsional potential. Table 1 provides the non-bonded Lennard-Jones 12-6 potential parameters and charges of all atom types in nylon. The inset of Table 1 illustrates the atom types of nylon 4. The geometric mixing rule  $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$  and  $\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$  is used to evaluate the non-bonded parameters between different atom types. Potential parameters for bond, angle, and dihedral are shown in Tables 2-4, respectively.

Table 1. Charge and 12-6 LJ parameters for all atom types of nylon

Atom type	q (e <sup>-</sup> )	$\epsilon$ (kcal · mol <sup>-1</sup> )	$\sigma$ (Å)
C	0.500	0.105	3.750
CT	0.080	0.066	3.500
CT1	-0.120	0.066	3.500
H	0.300	0.000	0.000
HC	0.060	0.030	2.500
N	-0.500	0.170	3.250
O	-0.500	0.210	2.960

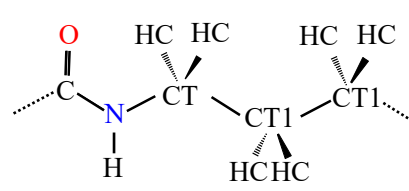


Table 2. Bond stretching potential,  $E_{bond} = \sum_{bonds} k(r - r_0)^2$

Bond type	$k$ (kcal · mol <sup>-1</sup> · Å <sup>-2</sup> )	$r_0$ (Å)
C-CT1	317.00	1.522
C-N	490.00	1.335
C-O	570.00	1.229
CT-CT1	268.00	1.529
CT-HC	340.00	1.090
CT-N	337.00	1.449
CT1-CT1	268.00	1.529
CT1-HC	340.00	1.090
H-N	434.00	1.010

<sup>1</sup> Corresponding Author; Email: [ling.liu@usu.edu](mailto:ling.liu@usu.edu)

Table 3. Angle bending potential,  $E_{angle} = \sum_{angles} k_{\theta}(\theta - \theta_0)^2$

Angle type	$k_{\theta}$ (kcal·mol <sup>-1</sup> ·radian <sup>-2</sup> )	$\theta_0$ (degree)
C-CT1-CT1	63.00	111.10
C-CT1-HC	35.00	109.50
C-N-CT	50.00	121.90
C-N-H	35.00	119.80
CT-CT1-CT1	58.35	112.70
CT-CT1-HC	37.50	110.70
CT-N-H	38.00	118.40
CT1-C-N	70.00	116.60
CT1-C-O	80.00	120.40
CT1-CT-HC	37.50	110.70
CT1-CT-N	80.00	109.70
CT1-CT1-HC	37.50	110.70
HC-CT-HC	33.00	107.80
HC-CT-N	35.00	109.50
HC-CT1-HC	33.00	107.80
N-C-O	80.00	122.90

Table 4. Torsional potential,

$$E_{torsion} = \frac{V_1}{2}[1 + \cos(\phi)] + \frac{V_2}{2}[1 - \cos(2\phi)] + \frac{V_3}{2}[1 + \cos(3\phi)] + \frac{V_4}{2}[1 - \cos(4\phi)]$$

Dihedral type	$V_1$ (kcal·mol <sup>-1</sup> )	$V_2$ (kcal·mol <sup>-1</sup> )	$V_3$ (kcal·mol <sup>-1</sup> )	$V_4$ (kcal·mol <sup>-1</sup> )
C-CT1-CT1-CT	-2.060	-0.313	0.315	0.000
C-CT1-CT1-HC	0.000	0.000	-0.100	0.000
CT-CT1-CT1-HC	0.000	0.000	0.300	0.000
CT1-C-N-CT	2.300	6.089	0.000	0.000
CT1-C-N-H	0.000	4.900	0.000	0.000
CT1-CT-N-C	0.000	0.462	0.000	0.000
CT1-CT-N-H	0.000	0.000	0.000	0.000
HC-CT-CT1-CT1	0.000	0.000	0.300	0.000
HC-CT-CT1-HC	0.000	0.000	0.300	0.000
HC-CT-N-C	0.000	0.000	0.000	0.000
HC-CT-N-H	0.000	0.000	0.000	0.000
HC-CT1-CT1-HC	0.000	0.000	0.300	0.000
N-C-CT1-CT1	1.173	0.189	-1.200	0.000
N-C-CT1-HC	0.000	0.000	0.000	0.000
N-CT-CT1-CT1	0.845	-0.962	0.713	0.000
N-CT-CT1-HC	0.000	0.000	0.464	0.000
O-C-CT1-CT1	0.000	0.000	0.000	0.000
O-C-CT1-HC	0.000	0.000	0.000	0.000
O-C-N-CT	0.000	6.089	0.000	0.000
O-C-N-H	0.000	4.900	0.000	0.000

**2. Effects of torsional disorder on thermal conduction:** We chose the single-chain nylon 4 and the  $2 \times 2$  nanofiber as two examples to demonstrate the effects of torsional disorder on thermal conduction. The torsional disorder was controlled by adjusting the dihedral potential in the OPLSAA force field. In the case with full dihedral potential, the torsional motion of polymer segments is restricted leading to more ordered chain structures. When the dihedral potential is neglected, however, the structures are more disordered. Evidences can be found in Figure S2(a), which shows less deviated dihedrals when the computation includes the dihedral potential. Figure S2(b) further establishes the correlation between structural order and thermal conductivity. For both the single-chain and  $2 \times 2$  nylon 4, thermal conductivity is found to be higher when the dihedral potential is considered (i.e. when the structure is more ordered). The most significant contribution of the present paper is to provide a feasible means to confine the torsional disorder by hydrogen bonds for improved thermal conductivities.

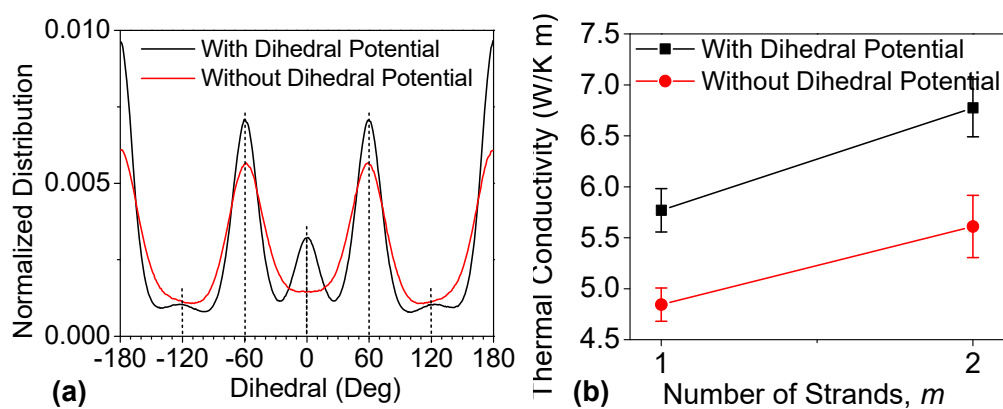


Figure S1. (a) Dihedral distributions of nylon4-20-1-1 computed with and without considering the dihedral potential in the force field. (b) Thermal conductivities of nylon4-20-1-1 and nylon4-20-2-1 computed with and without the dihedral potential.

### 3. Normalized distribution of 12 types of dihedrals in nylon2-20-*m*-1

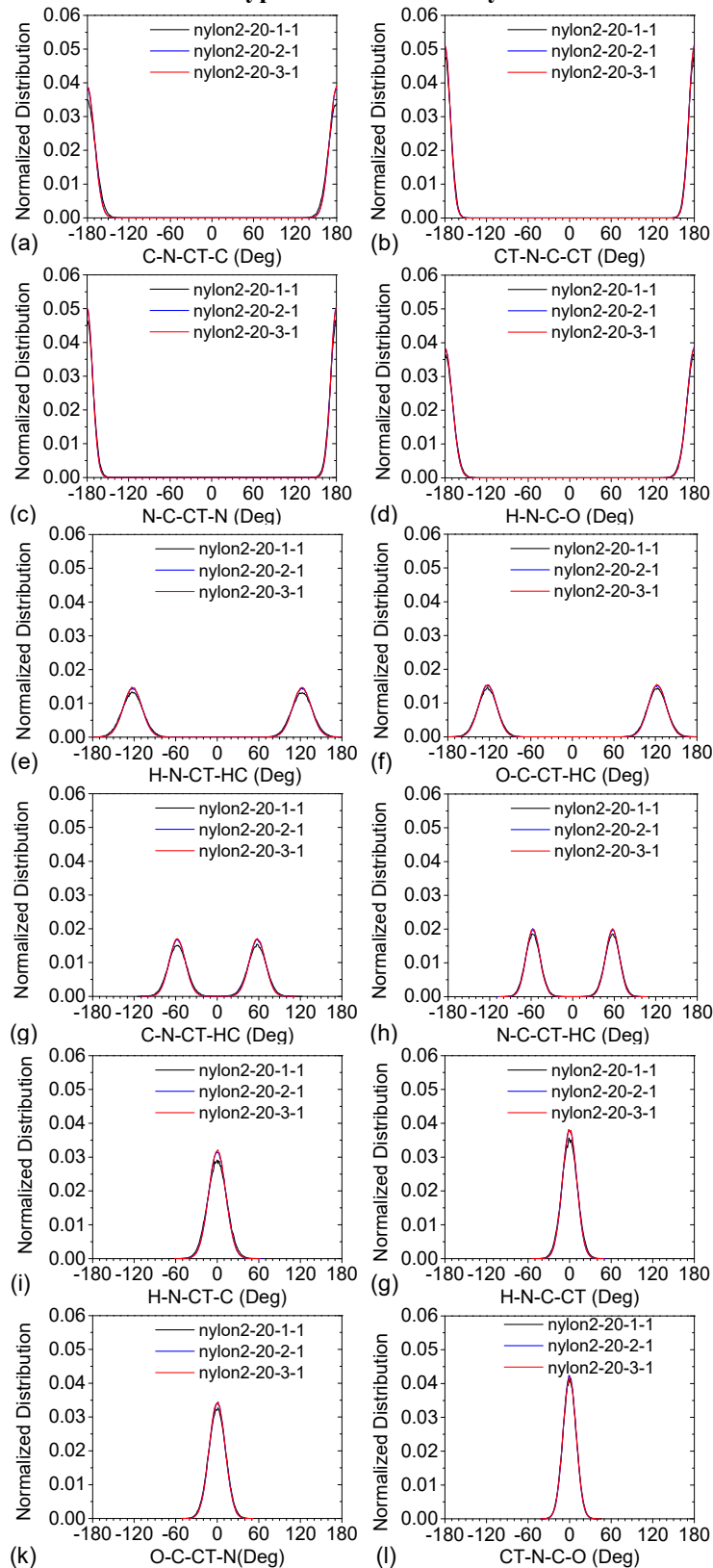


Figure S2. Normalized distribution of dihedrals.

#### 4. Time history of 12 types of dihedrals in nylon2-20-*m*-1

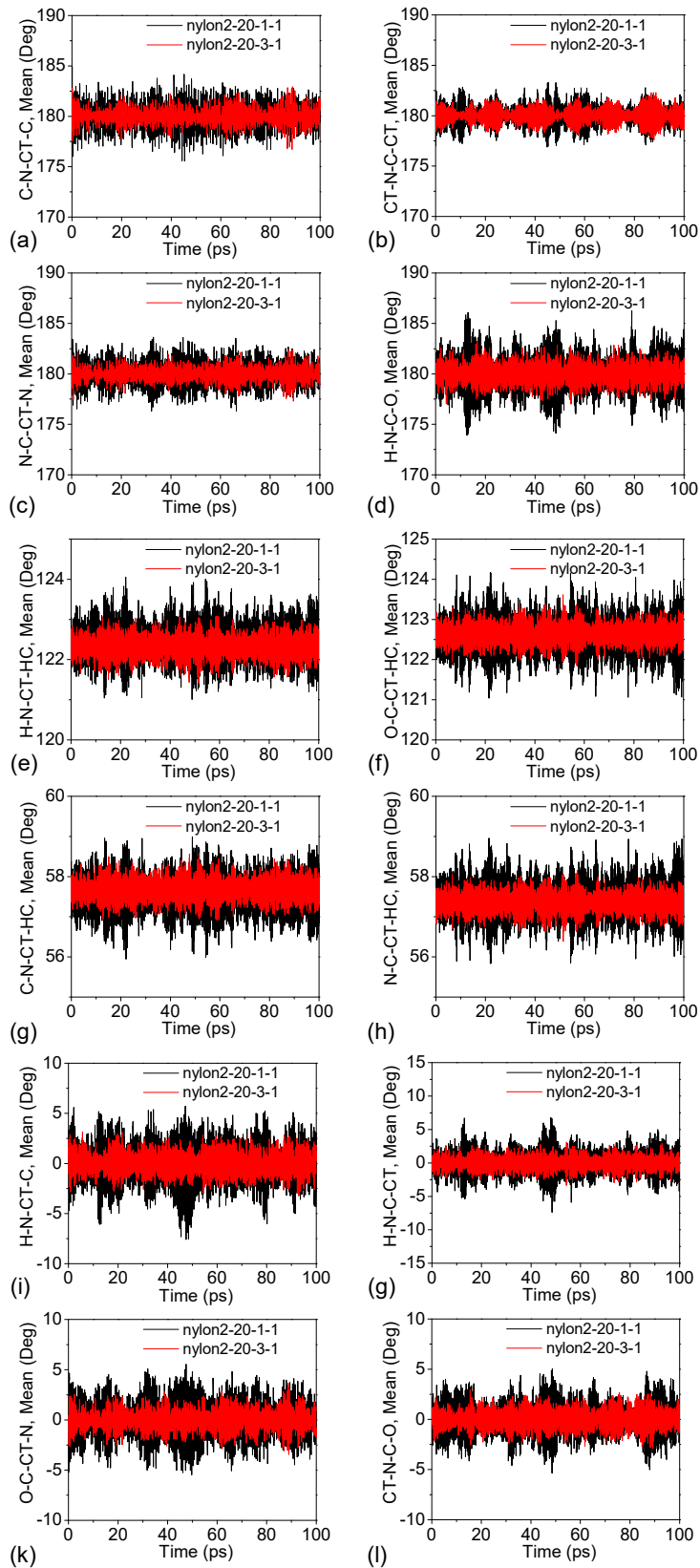


Figure S3, Mean value of dihedral angles versus time.

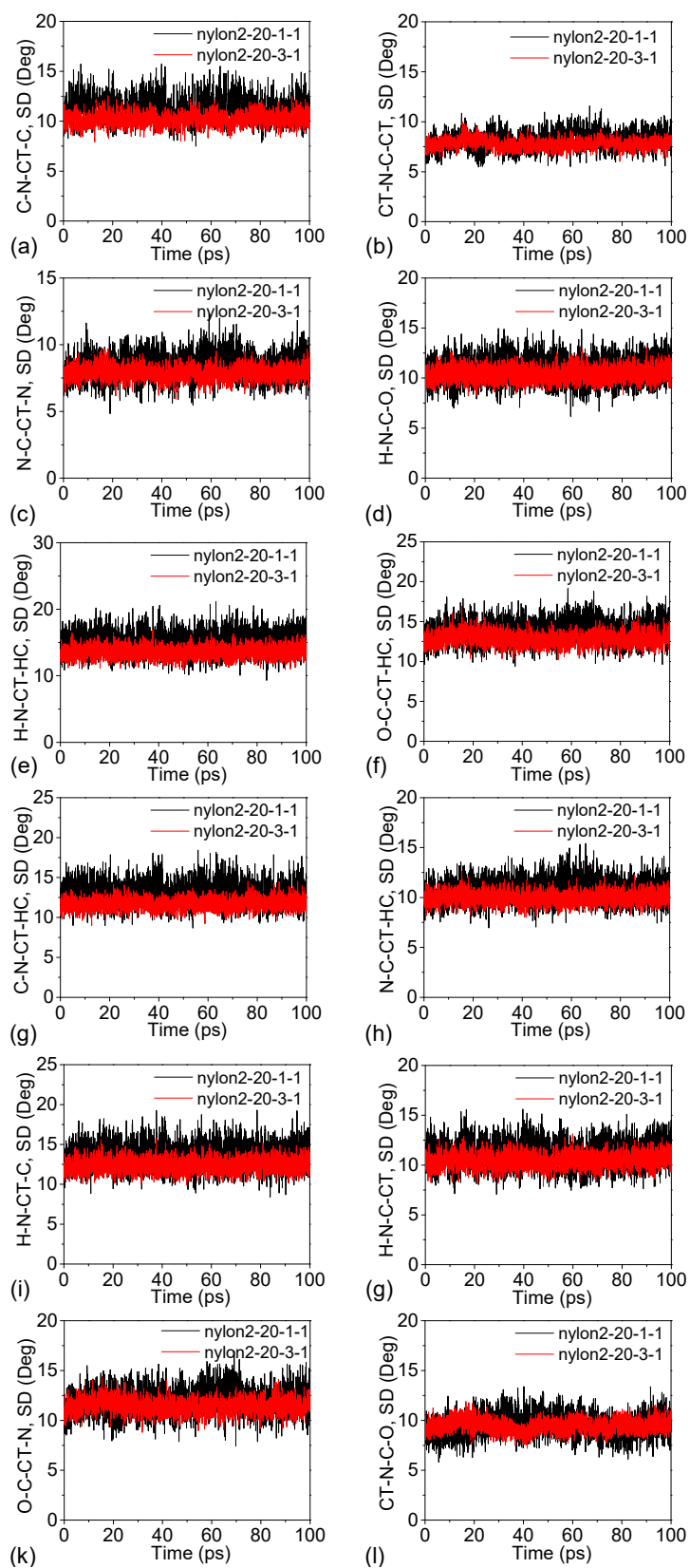


Figure S4. Standard deviation of dihedral angles versus time.

## References

- 1 M. L. P. Price, D. Ostrovsky, and W. L. Jorgensen, *J Comput Chem*, **22**, 1340 (2001).
- 2 W. L. Jorgensen, D. S. Maxwell, and J. TiradoRives, *J Am Chem Soc*, **118**, 11225 (1996).