Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information (ESI)

The Effect of Block Ratio on the Thermal Conductivity of Amorphous Polyethylene-Polypropylene (PE-PP) Diblock Copolymers

Xingfei Wei*, [a] and Tengfei Luo [a, b]

[a] Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA

[b] Center for Sustainable Energy at Notre Dame, University of Notre Dame, Notre Dame, Indiana 46556, USA

* Corresponding author: Mr. Xingfei Wei. E-mail: xwei2@nd.edu. Tel: + 15749046870.

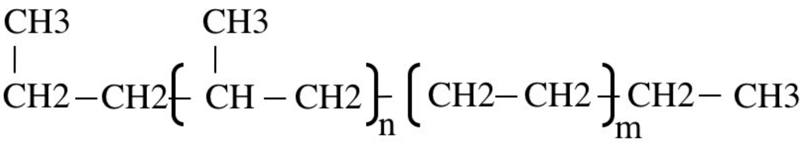
1. Simulation Force Field Parameters

Figure S1 shows the molecular configuration of the polyethylene-polypropylene (PE-PP) diblock copolymer with a united atom model. The van der Waals (vdW) pairwise interaction parameters are listed Table S1. The cross interaction parameters are calculated by the geometric mixing rule, as following.

$$\epsilon_{ij} = \sqrt{e_i * e_j} \tag{1}$$

$$\sigma_{ij} = \sqrt{\sigma_i * \sigma_j} \tag{2}$$

The bond and angle are in both harmonic style. The bond type and interaction parameters are listed in Table S2. The angles' types and interaction parameters are listed in Table S3. The dihedral is in OPLS style, and the special bonds parameter in the simulation is set at lj/cut 0 0 0.5. The dihedral parameters are listed in Table S4.



$$\overset{\text{CH3}}{\overset{|}{\text{CH2}}}-\text{CH2}\left[\overset{\text{CH3}}{\overset{|}{\text{CH}}}-\text{CH2}\right]_n\left[\text{CH2}-\text{CH2}\right]_m\text{CH2}-\text{CH3}$$

Figure S1. The structure of PE-PP block copolymers. The total number of monomers is kept at 100, n+m=98. The PP portion (n) is tuned to generate different block ratios.

Table S1. Pair interaction parameters.

Pairs	Pair style	ϵ (kcal/mol)	σ (Å)	Cutoff (Å)
CH3-CH3	lj/cut/coul/cut	0.175	3.905	10
CH2-CH2	lj/cut/coul/cut	0.118	3.905	10
CH-CH	lj/cut/coul/cut	0.080	3.850	10

Table S2. Bond type and parameters.

Bonds	Bond style	r_0 (Å)	K (kcal/mol/Å^2)
All the bonds	harmonic	1.526	260.0

Table S3. Angle type and parameters.

Angles	Angle style	$\boldsymbol{\theta}_0$ (degree)	K (kcal/mol/radian^2)
CH2-CH2-CH2	harmonic	112.4	63.0
CH-CH2-CH	harmonic	112.4	63.0
CH2-CH-CH2	harmonic	112.4	63.0
CH2-CH2-CH3	harmonic	112.4	63.0
CH2-CH-CH3	harmonic	112.4	63.0
CH3-CH-CH3	harmonic	111.5	63.0

Table S4. Dihedral types and parameters.

Dihedrals	Dihedral style	K_1 (kcal/mol)	K_2 (kcal/mol)	K_3 (kcal/mol)	K_4 (kcal/mol)
CH2-CH2-CH2-CH2	opls	-3.40	1.25	-2.50	0.00
CH2-CH2-CH2-CH3	opls	-3.40	1.25	-2.50	0.00
CH-CH2-CH2-CH2	opls	-3.40	1.25	-2.50	0.00
CH2-CH-CH2-CH2	opls	-3.40	1.25	-2.50	0.00
CH-CH2-CH-CH2	opls	-2.50	1.25	3.10	0.00
CH-CH2-CH-CH3	opls	-2.50	1.25	3.10	0.00
CH3-CH2-CH-CH3	opls	-2.50	1.25	3.10	0.00

2. System at Equilibrium

We use the 50% PP content diblock copolymer as an example to show the equilibrium of the model. The PE-PP copolymer systems are equilibrated at NPT ensemble, before NVT and NVE ensemble. Figure S2 show the total energy and the pressure of the system is equilibrium after 10 ns. The average radius of gyration (R_g) of 400 copolymer chains is at equilibrium after 10 ns, Fig. S3, which represents the conformation of the molecules are at equilibrium.

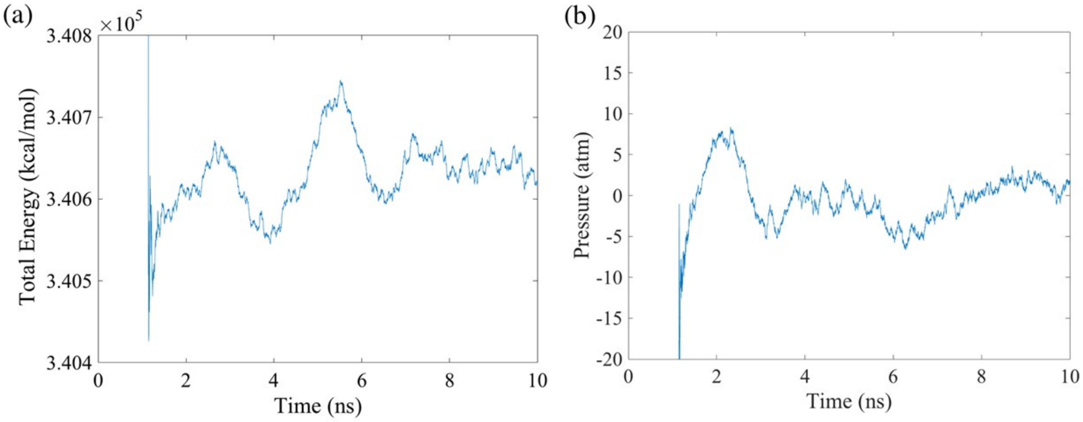


Figure S2. (a) The total energy of the system equilibrium at 10 ns. (b) The pressure of the system stabilized at 1 atm at 10 ns.

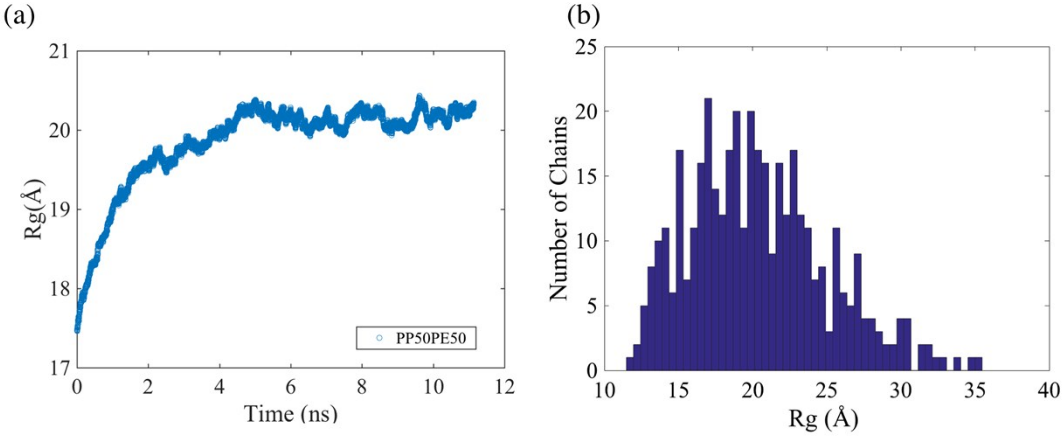


Figure S3. (a) The average R_g converged to ~ 20.4 Å after 10 ns of simulation. (b) The distribution of the number of copolymer chains at different R_g.

3. Number of Polymer Chain Effect

The $PE_{50}PP_{50}$ diblock polymer with 50 PE monomers and 50 PP monomers is used as an example to study the chain number effect. The average R_g is well converged when the chain number is above 100, Fig. S4 (a). The average value of the thermal conductivity converges after the chain number reaches 400, but all the thermal conductivity values are within error bar difference, Fig. S4 (b). The most important observation is that the standard deviation of the thermal conductivity converges when the chain number is larger than 200, and for the chain number at 100 the average value is close to the other data points but the standard deviation is significantly higher than the other samples, Fig. S4 (b). Therefore, we can conclude that the sample size can not affect the average property measurement, but the uncertainty of the measurement will increase, which can further be reduced by some methods such as multiple sampling.

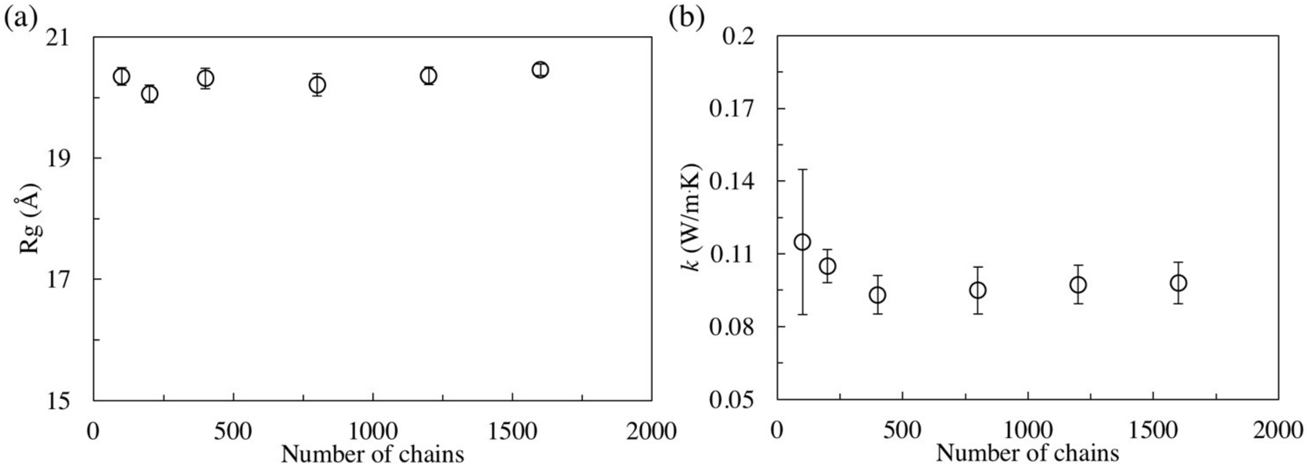


Figure S4. (a) The effect of the number of polymer chains in the simulation box on the average R_g. (b) The thermal conductivity effect from the number of polymer chains in the simulation box.

4. Heat Flux Decomposition

By calculating the energy flux within the PP portion and within the PE portion of the block copolymers, the thermal conductivity can be decomposed into thermal conductivity contributed from PP (PP-k) and thermal conductivity contributed from PE (PE-k). Applying the heat flux calculation on different groups, the overall heat flux (group all), the PE-PE + ½ PE-PP cross interaction heat flux (group PE) and the PP-PP + ½ PE-PP cross interaction heat flux (group PP) can be calculated separately. The overall heat flux is the sum of the PE contribution (PE-PE + ½ PE-PP cross interaction) and PP contribution (PP-PP + ½ PE-PP cross interaction). Figure S5 shows that the total heat flux is decomposed into the heat flux carried by the PP and PE portions. Figure S6 shows that the calculated heat flux tally is well converged to the thermostat tally heat flux (heat sink and heat source).

The total force on a particle is the sum of the non-bonding force (i.e., vdW and electrostatic), dihedral force, angle force, and bond force. The heat flux through the PE and PP portions are further decomposed into bonding (bond + angle + dihedral) and non-bonding contributions for each portion. Figure S7 shows the heat flux decomposition for the PE portion at a PP content of 50%. Figure S8 shows the heat flux decomposition for the PP portion at the PP content of 50%.

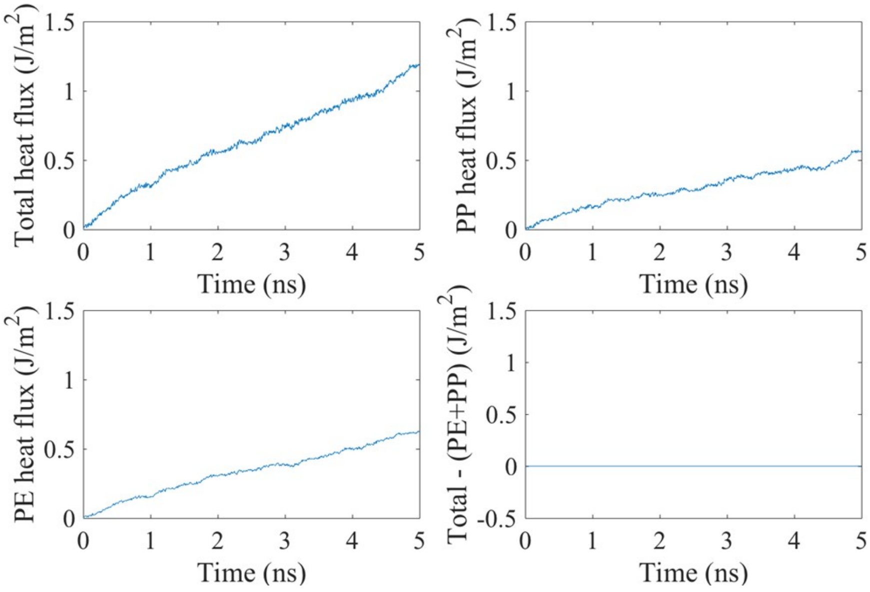


Figure S5. The total heat flux tally from the calculation of the sum of the forces multiply the velocities, and the decomposition of the total heat flux in to the PE and PP contributions for the PE-PP diblock copolymer at the PP content of 50%.

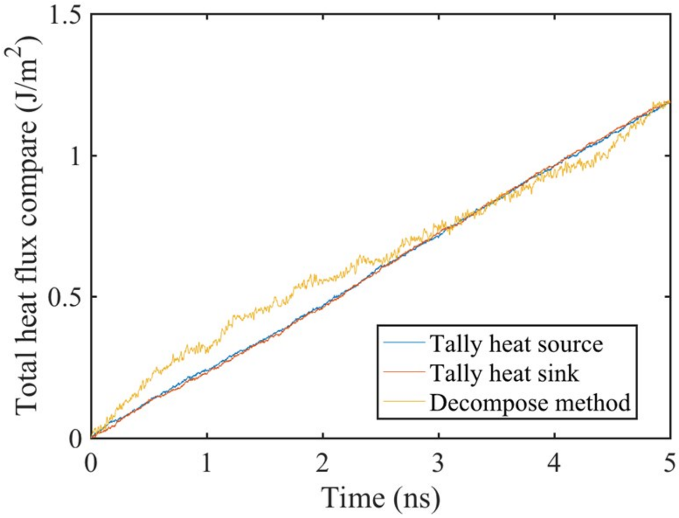


Figure S6. The heat flux tally comparison between the calculated heat flux in the decomposition method (yellow line), the energy input tally at the heat source (blue line) and the energy output tally at the heat sink (red line).

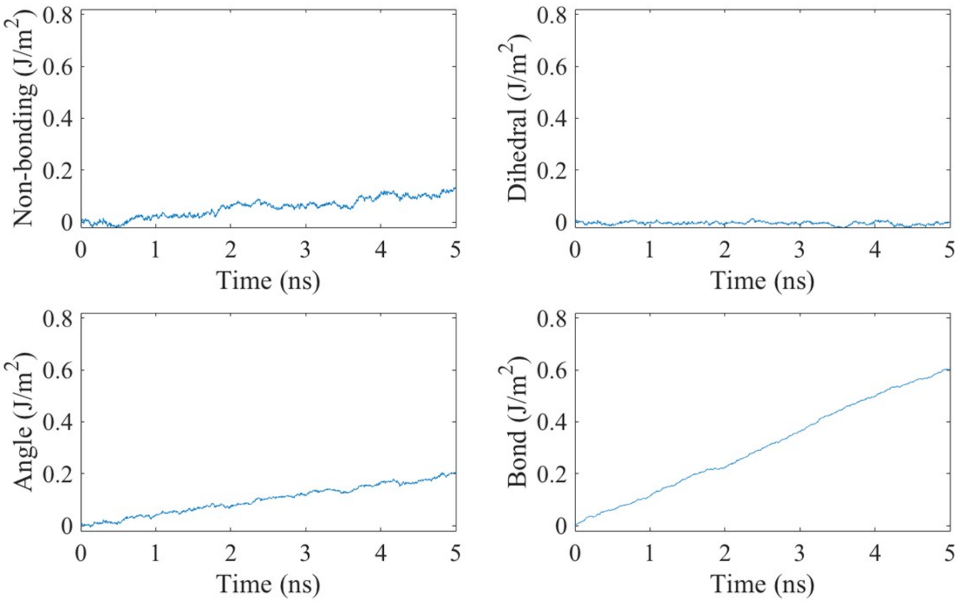


Figure S7. The decomposition of the total heat flux in the PE portion to non-bonding, dihedral, angle and bond contributions for the PE-PP diblock copolymer at the PP content of 50%.

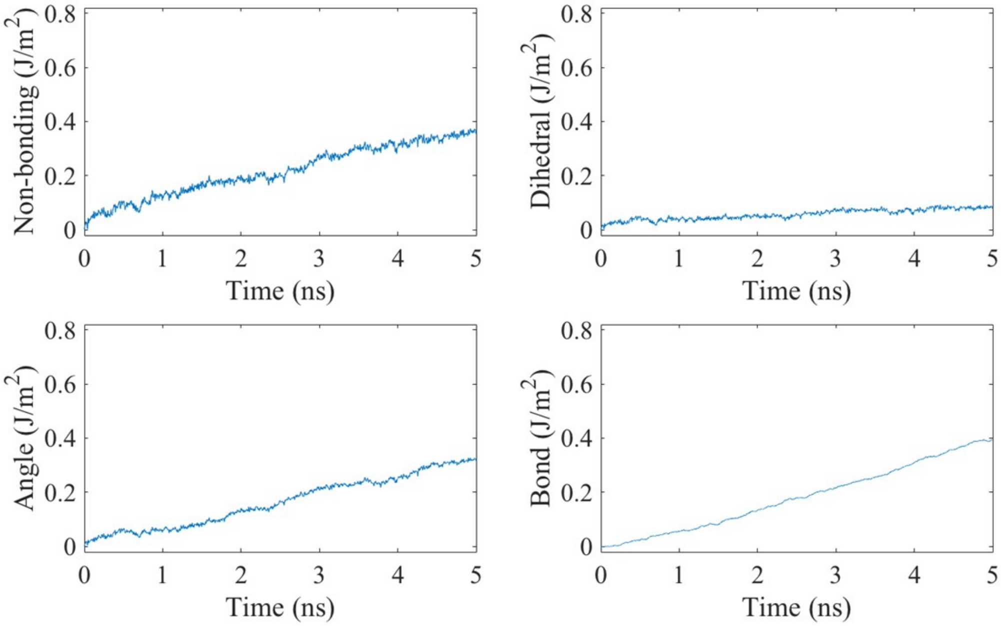


Figure S8. The decomposition of the total heat flux in the PP portion to non-bonding, dihedral, angle and bond contributions for the PE-PP diblock copolymer at PP content 50%.