Modifying thermal transport in electrically conducting polymers: Effects of stretching and combining polymer chains

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Abstract
If their thermal conductivity can be lowered, polyacetylene (PA) and polyaniline(PANI) offer examples of electrically conducting polymers that can have potential use as thermoelectrics. Thermal transport in such polymers is primarily influenced by bonded interactions and chain orientations relative to the direction of heat transfer. We employ molecular dynamics simulations to investigate two mechanisms to control the phonon thermal transport in PANI and PA, namely, (1) mechanical strain and (2) polymer combinations. The molecular configurations of PA and PANI have a significant influence on their thermal transport characteristics. The axial thermal conductivity increases when a polymer is axially stretched but decreases under transverse tension. Since the strain dependence of the thermal conductivity is related to the phonon scattering among neighboring polymer chains, this behavior is examined through Herman's orientation factor that quantifies the degree of chain alignment in a given direction. The conductivity is enhanced as adjacent chains become more aligned along the direction of heat conduction but diminishes when they are orthogonally oriented to it. Physically combining these polymers reduces the thermal conductivity, which reaches a minimum value for a 2:3 PANI/PA chain ratio.

Keywords
Conducting polymers, Polymers, Thermal conductivity, Phonons, Heat conduction, Heat transfer, Molecular dynamics, Thermoelectric effects, Chemical bonds, Thermal properties

Disciplines
Heat Transfer, Combustion

Comments

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Modifying thermal transport in electrically conducting polymers: Effects of stretching and combining polymer chains

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(Received 30 October 2011; accepted 28 December 2011; published online 26 January 2012)

If their thermal conductivity can be lowered, polyacetylene (PA) and polyaniline (PANI) offer examples of electrically conducting polymers that can have potential use as thermoelectrics. Thermal transport in such polymers is primarily influenced by bonded interactions and chain orientations relative to the direction of heat transfer. We employ molecular dynamics simulations to investigate two mechanisms to control the phonon thermal transport in PANI and PA, namely, (1) mechanical strain and (2) polymer combinations. The molecular configurations of PA and PANI have a significant influence on their thermal transport characteristics. The axial thermal conductivity increases when a polymer is axially stretched but decreases under transverse tension. Since the strain dependence of the thermal conductivity is related to the phonon scattering among neighboring polymer chains, this behavior is examined through Herman’s orientation factor that quantifies the degree of chain alignment in a given direction. The conductivity is enhanced as adjacent chains become more aligned along the direction of heat conduction but diminishes when they are orthogonally oriented to it. Physically combining these polymers reduces the thermal conductivity, which reaches a minimum value for a 2:3 PANI/PA chain ratio. © 2012 American Institute of Physics. [doi:10.1063/1.3678848]

I. INTRODUCTION

Delocalized electrons associated with the sp2-hybridized carbon atoms contained within the backbone of conjugated electrically conducting (EC) polymers such as PA and PANI have a high mobility. These electrons serve as the primary charge carriers for electrical conduction,1 which makes them suitable for thermoelectric applications.2,3 The electron delocalization and, hence, the electrical conductivity σ can be further enhanced by doping them with various materials. Since the charge transport of delocalized electrons in an EC polymer has a different mechanism than the free electron drift in metals, their electrical conductivity is only weakly correlated with their thermal conductivity κ. Hence, while the doping of EC polymers increases σ, it does not significantly influence κ.2,4

Since the electron contribution to heat conduction is typically insignificant in EC polymers, we only consider the more relevant contribution of phonon transport. Individual polymer chains can have a relatively high phonon thermal conductivity κp as compared to their bulk amorphous volumes.5 In contrast with individual chains, the highly twisted and irregular bulk macromolecular chain arrangements serve to enhance phonon scattering and shorten the phonon mean free paths, thus reducing κp.6 While the literature discusses means to increase κp for polymers,5,6 few strategies have been offered for ways to lower it.7 Lowering κp is essential, if EC polymers are to find widespread use in thermoelectrics,8 thermal barrier coatings,9 and phase change memory technology.10

Unlike crystals, polymer chains experience both bonded and nonlinear anharmonic nonbonded interactions.7 Hence, the mechanism that reduces the lattice thermal conductivity of strained crystals11–13 fails to explain the corresponding influence of stretching on thermal transport in polymers. We employ atomistic simulations to understand how phonon thermal transport in the EC polymers (PANI and PA) can be modified when (1) they are subject to axial and transverse strains, or (2) their polymer chains are physically mixed.

II. COMPUTATIONAL METHODOLOGY

A. Nonequilibrium molecular dynamics simulations

Molecular dynamics simulations have been used to investigate the chain configuration of bulk polymers under applied strain.14–17 We employ nonequilibrium molecular dynamics (NEMD) to determine the thermal conductivity of strained PANI and PA using the LAMMPS code.18 Three systems are considered, namely, (1) pure amorphous PANI in emeraldine base form,19 (2) pure amorphous PA in trans-isomeric form, and (3) combinations of PANI and PA containing different numbers of chains of each polymer. The number of atoms and the dimensions of the equilibrated systems used to simulate unstrained PANI and PA, and the different PANI/PA mixture compositions that are considered are provided in Table I. Periodic boundary conditions are imposed along all three coordinate directions. Both the amorphous PANI and PA systems contain 80 chains, while their 1:1 mixture contains 40 chains of each polymer. Each PANI and PA chain contains 24 carbon atoms. The chain structures are generated with XenoView (Ref. 20) for an initial density ρ at T = 300 K and P = 1 atm.
TABLE I. The dimensions of the simulated systems and the number of atoms present in them are listed. The percentage of PANI corresponds to the number of PANI chains relative to the total number of polymer chains in the simulation domain. The system dimensions reported are values obtained upon equilibration of the polymers.

<table>
<thead>
<tr>
<th>% of PANI</th>
<th>X (Å)</th>
<th>Y (Å)</th>
<th>Z (Å)</th>
<th>No. of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 (Pure PANI)</td>
<td>35.42</td>
<td>35.42</td>
<td>35.42</td>
<td>3840</td>
</tr>
<tr>
<td>87.5</td>
<td>35.63</td>
<td>35.63</td>
<td>35.63</td>
<td>3860</td>
</tr>
<tr>
<td>75</td>
<td>35.67</td>
<td>35.67</td>
<td>35.67</td>
<td>3880</td>
</tr>
<tr>
<td>62.5</td>
<td>35.95</td>
<td>35.95</td>
<td>35.95</td>
<td>3900</td>
</tr>
<tr>
<td>50 (1:1 mixture)</td>
<td>35.90</td>
<td>35.90</td>
<td>35.90</td>
<td>3920</td>
</tr>
<tr>
<td>37.5</td>
<td>36.19</td>
<td>36.19</td>
<td>36.19</td>
<td>3940</td>
</tr>
<tr>
<td>25</td>
<td>36.12</td>
<td>36.12</td>
<td>36.12</td>
<td>3960</td>
</tr>
<tr>
<td>12.5</td>
<td>36.37</td>
<td>36.37</td>
<td>36.37</td>
<td>3980</td>
</tr>
<tr>
<td>0 (Pure PA)</td>
<td>36.11</td>
<td>36.11</td>
<td>36.11</td>
<td>4000</td>
</tr>
</tbody>
</table>

(where $\rho_{\text{PANI}} = 1.3 \text{ g cm}^{-3}$ and $\rho_{\text{PA}} = 1.16 \text{ g cm}^{-3}$).\textsuperscript{19, 21} The parameters for the polymer consistent force field (PCFF) that describe the bonded and nonbonded interactions are obtained from the literature,\textsuperscript{19, 20} details about which are provided in the Appendix. The VMD package\textsuperscript{22} is used to visualize the response of the polymers to applied strains.

The energy of each system is first minimized using the conjugate gradient technique.\textsuperscript{18} The minimized structure is then initialized at 300 K. This is followed by a two-step process where the system is: (1) first heated over 0.1 ns to a temperature much higher than the glass transition temperature ($T_g$), i.e., from $T = 300$ K to $T = 1000$ K (for PANI, $T_g = 493$ K; for PA, $T_g = 473$ K), and (2) then cooled back to 300 K over 0.1 ns under a canonical (NVT) ensemble using a Langevin thermostat with a coupling time of 0.1 ps. This annealing and tempering relaxes the molecules and removes any bond symmetry that could have been an artifact produced through polymer construction.

Next, the system is equilibrated under isothermal-isobaric conditions ($NPT$ with $T = 300$ K and $P = 1$ atm) followed by the $NVT$ and $NVE$ ensembles, each for 0.2 ns, respectively. The equilibrated systems are strained from an initial zero engineering strain rate $\varepsilon$ in five increments of $2 \times 10^{-10}$ s$^{-1}$ to $10 \times 10^{-10}$ s$^{-1}$. These strains are applied along both the axial ($x$) and transverse ($y$) directions through separate simulations. All strained structures are allowed to equilibrate for 0.3 ns under the $NVT$ ensemble before thermal conductivity calculations are performed.

B. Phonon thermal conductivity

The axial thermal conductivity, $\kappa_x$, is determined by employing a standard NEMD technique.\textsuperscript{23} A source of dimensions $0.7084 (x) \times 35.42 (y) \times 35.42 (z)$ Å placed at the center of the system heats two sinks that are located at both x-wise boundaries (with dimensions equal to half the x-wise thickness of the heat source), as shown in Fig. 1. The figure also shows how the temperature gradient across the material is calculated over linear sections of the steady-state temperature distribution. This temperature gradient is sampled over the final 1 ns of the 5 ns NEMD simulation. A temporal average is employed to determine its steady-state value and the net heat flux transferred between the heat source and its sinks. Thereafter, the thermal conductivity is calculated based on Fourier’s heat conduction law.\textsuperscript{24} More extensive details about the simulation methodology are available in the supplementary material.\textsuperscript{25}

III. RESULTS AND DISCUSSIONS

A. The effect of strain on thermal conductivity

Figure 2(a) presents $\kappa_p$ at different uniaxial strains for PANI, PA, and a 1:1 PANI/PA mixture. Its value increases with increasing strain but the rate of increase in $\kappa_p$ successively decreases. The thermal conductivities of unstrained PANI and PA that are thus obtained (0.1 and 0.08 Wm$^{-1}$ K$^{-1}$, respectively) are compared with reported experimental measurements (0.11 and 0.38 Wm$^{-1}$ K$^{-1}$ (Refs. 26 and 27)). While the two PANI values are in good agreement, the ones for PA, for which the cited measurement is for a 0.89 μm thin film,\textsuperscript{27} are not, where the simulated value is much lower. The thermal conductivity is often lower at the nanoscale, as for our simulations, than at the microscale, as for thin films, since the energy losses due to phonon scattering at the system boundaries are enhanced as the system dimensions are reduced.\textsuperscript{26, 29} We also show later that the helical structure of PA lends itself to a lower $\kappa_p$ in contrast to the more planar PANI.

Large tensile strains in crystal lattices reduce van der Waals interactions and hence the phonon thermal...
conductivity. However, phonon transport in polymers occurs through both (1) intrachain energy exchanges that involve relatively stiff covalent bonds in the polymer backbone and (2) interchain heat transfer through weak van der Waals interactions that involve softer force constants between the constituent atoms of two different chains. Hence, unlike for crystal lattices, the major phonon contribution to heat transfer in polymers is through the bonded interactions. The increase in $\kappa_p$ shown in Fig. 2(a) occurs due to the growing structural ordering that is induced in the polymers as these are strained. The polymer chains that are highly twisted and randomly oriented in the initial unstretched amorphous bulk provide a structure that favors phonon-phonon scattering, thus lowering the thermal conductivity. In contrast, straining the material incrementally aligns the chains along the direction of stretch. Chain alignment lowers phonon scattering and improves energy transport through the polymer backbones, thereby increasing $\kappa_p$. Similarly, we find that when these polymer chains are compressed (not shown here), $\kappa_p$ decreases, which validates this hypothesis. However, since the number of polymer chains in the system is finite, there is an upper limit to the enhancement of $\kappa_p$. The increasing molecular alignment gradually tapers off at relatively large values of mechanical strain, and phonon heat conduction is no longer improved through polymer stretching. Thus, Fig. 2(a) also shows that the rate of increase in $\kappa_p$ decreases at higher strain rates.

Figure 2(b) presents the influence of transverse strain (along the $y$-direction) on $\kappa_p$. This conductivity decreases as the transverse strain increases. Imposing $\varepsilon = 33.6\%$ reduces the thermal conductivities of PANI, PA, and their 1:1 mixture by 24.7\%, 11.6\%, and 23.44\%, respectively, with respect to their corresponding unstrained values. A transverse strain induces additional anisotropy by orienting the polymer chains orthogonal to the direction of thermal transport, thus diminishing axial heat conduction. Here, instead of intrachain bonded interactions, interchain intermolecular collisions mainly influence the energy transfer along the $x$-direction. The larger the transverse strain is, the lower the value of $\kappa_p$ is. The rate of decrease in $\kappa_p$ is again lowered at larger transverse strains, indicating saturation in the alignment of polymer chains in a similar manner to the results for axial stretching.

B. The effect of polymer combination on thermal conductivity

Figure 2(a) shows that the thermal conductivity of a PANI-PA combination is lower than for either of the pure polymers. Combining these polymers produces a physical mismatch between the characteristic frequencies for the thermal vibrations and intermolecular collisions associated with their two different polymer backbones. One polymer can thus be thought to behave as an impurity within the other, which enhances phonon scattering just as the differences in the masses and force constants of impurity atoms within a bulk material diminish thermal transport. The thermal conductivities of several unstrained polymer combinations are presented in Fig. 3, which shows that physical combinations of PANI and PA lower $\kappa_p$ below its value for either of the two pure polymers. The conductivity is lowest for a combined heterogeneous polymer that contains a 2:3 PANI:PA chain ratio. We have previously shown for a binary mixture of crystalline solids that such a behavior is related to their molar mass fractions. While the mass dependence of thermal
conductivities for the amorphous polymer combinations do not conform to the analytical expression for crystalline materials due to differences in the major contributors to phonon thermal transport, both systems exhibit a minimum $\kappa_p$ for a specific composition of the binary mixture.

C. Herman’s orientation factor and chain alignment

Polymer chain alignment in the direction of heat transfer can be characterized through Herman’s orientation factor $f_i$. For the $i$th polymer chain, it is represented as

$$f_i = \frac{3}{2} \left( \frac{1}{B_i} \sum_{j=1}^{B_i} \cos^2 \theta_j \right) - \frac{1}{2}, \quad \text{where} \quad -\frac{1}{2} \leq f_i \leq 1.$$  \hspace{1cm} (1)

In Eq. (1), $\theta_j$ denotes the angle between the $j$th bond in the backbone of the $i$th polymer and the $x$ axis, and $B_i$ denotes the total number of bonds in the backbone of the $i$th polymer chain. When (1) $f_i = 1$, the chains are fully aligned, i.e., all chains are oriented along the $x$ axis, (2) $f_i = 0$, the system is isotropic with no preferential alignment in any particular direction, and (3) $f_i = -0.5$, all chains are aligned transversely and perpendicular to the $x$ axis. The overall orientation factor $f$ for the entire system is calculated by averaging $f_i$ for all polymer chains in the system.

Figure 4(a) shows that axial straining increases $f$ for PANI but that the overall alignment of PA is not significantly influenced by axial strain. The effect of increasing chain alignment on $\kappa_p$ for both polymers is presented in Fig. 4(b). In accord with Fig. 4(a), $\kappa_p$ increases with increasing PANI chain alignment but straining produces a smaller influence on the PA

![FIG. 5.](image)

**FIG. 5.** (a) Variation of $f$ with respect to the tensile strain in the transverse direction for PANI and PA. (b) Variation of $\kappa_p$ with respect to $f$ for different PANI and PA transverse strains. For (b), error bars are determined in a similar manner as for Fig. 2.

![FIG. 6.](image)

**FIG. 6.** Representative structures of PA and PANI molecule backbones obtained from our simulations. The backbone of PA is helical, while the PANI backbone is more planar.
chain alignment and thus the hypothesis that increasing axial strain improves the polymer conductivity due to the lower degree of induced chain alignment. Taken together, Figs. 4(a) and 4(b) again validate the polymer chain alignment and thus \( \kappa_p \). Transverse strain decreases the axial polymer chain alignment as illustrated in Fig. 5(a). The figure shows that increasing transverse strain reduces the axial chain alignment for PANI but again PA is not as significantly influenced. Consequently, as expected, we observe from Fig. 5(b) that the reduction in the alignment of the PANI chains lowers \( \kappa_p \) but the corresponding value for PA is not as significantly influenced.

These results consistently demonstrate that the correlations between strain and chain alignment, and in effect the thermal conductivity, are significantly weaker for PA than for PANI. We explain this by emphasizing the differences in their molecular configurations. Figure 6 presents representative structures of unstrained individual PA and PANI chains obtained from the simulations. \textit{Ab initio} calculations predict that helical configurations are more energetically stable than planar orientations for PA chains, which is also confirmed by our simulations that corroborate the preferred helical form. The different contributions to the total intramolecular energy \( E_{\text{molecule}} \) for equilibrated and unstrained pure PA and PANI systems listed in Table II show a significantly higher \( E_{\text{molecule}} \) for PA (18 151.4 Kcal mol\(^{-1} \)) than for PANI (7923.5 Kcal mol\(^{-1} \)). The differences in \( E_{\text{molecule}} \) for PANI and PA mainly arise from their dissimilar torsional energies. That for PA is higher due to its helical configuration as compared to that for the more planar PANI. Consequently, the straining of PA does not cause appreciable chain stretching and, thus, does not also improve its chain alignment. On the contrary, PANI reshapes into an elongated structure when stretched, promoting overall chain alignment. The nonplanar PA chain configuration also explains the lower intrinsic thermal conductivity of pure PA as compared to pure PANI.

### IV. SUMMARY

Phonon thermal transport can be modified in EC polymers by applying mechanical strain or through binary polymer mixing. Applying an axial tensile strain increases chain alignment in a polymer that improves intrachain phonon transport. While nonbonded interactions are typically reduced by increasing tensile strain in crystals, these have a smaller significance in EC polymers where phonon transport is instead more significantly affected by chain alignment. Improving axial chain alignment, e.g., by mechanical straining, increases the overall axial thermal conductivity. Transverse strain promotes the alignment of polymer chains orthogonal to the direction of axial heat transfer and, thus, reduces the axial thermal conductivity by localizing phonons in neighboring polymer chains. Since the differences in atomic masses and bond force constants are typically responsible for reducing the thermal transport in a binary system, impurities with masses and bond spring constants very different from the bulk material can induce a substantial reduction in the thermal conductivity. Hence, physically combining polymers and exploiting the mismatch between their different characteristic phonon and intermolecular collision frequencies can also be used to lower the overall thermal conductivity. The preferential helical configuration of PA chains results in their lower intrinsic thermal conductivity as compared to PANI which contains relatively more planar polymer backbones. This helicity also diminishes the influence of strain on thermal transport for PA in comparison to the more planar PANI molecules.

### ACKNOWLEDGMENTS

We thank Professor Aman Haque, Department of Mechanical and Nuclear Engineering, Pennsylvania State University, for introducing us to the EC polymers. G.B. thanks Professor Eugene Joseph, Institute for Critical Technology and Applied Science, Virginia Tech, for explaining the fundamentals of polymer stretching. We thank the Virginia Tech Department of Engineering Science and Mechanics for use of its Linux Compute Cluster.

### APPENDIX: DESCRIPTION OF THE FORCE FIELD EMPLOYED FOR THE MOLECULAR DYNAMICS SIMULATIONS

We use a class II force field, polymer consistent force field (PCFF), in which the total potential energy of the polymer

\[
E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{out-of-plane}} + E_{\text{cross-coupling-term}} + E_{\text{nonbonded}},
\]

\[(A1)\]

\[
E_{\text{bond}} = \sum c_1 (l - l_0)^2 + c_2 (l - l_0)^3 + c_3 (l - l_0)^4,
\]

\[(A2)\]

\[
E_{\text{angle}} = \sum d_1 (\theta - \theta_0)^2 + d_2 (\theta - \theta_0)^3 + d_3 (\theta - \theta_0)^4.
\]

\[(A3)\]
for the effect of one deformation on the other, e.g., the influence of bond stretching on angle bending. These are calculated from Eqs. (A7)–(A12). In these relations, \( \theta_0, f_0, \theta_0, g_1, g_2, g_3, g_1, g_2, g_3, h, h', \) and \( k_{\text{aa}} \) are all constants. The nonbonded interactions are given by \( E_{\text{nonbonded}} \) which is the sum of contributions from Coulombic \( (E_{\text{Coulomb}}) \) and \( \text{van der Waals} (E_{\text{vdw}}) \) interactions. For Coulombic interactions, as shown in Eq. (A14), \( q_i \) and \( q_j \) represent the partial charges of atoms separated by an interatomic distance of \( r_{ij} \). For calculating long range Coulombic interactions, a particle-particle particle-mesh\(^{16}\) algorithm is used. The \( \text{van der Waals} \) interactions are calculated in the form of a 6-9 Lennard-Jones (LJ) potential, as shown in Eq. (A16). Here, the size parameter \( \sigma_{ij} \) is the radial distance \( r_{ij} \) between the centers of atoms \( i \) and \( j \) at which the potential is zero and \( \epsilon_{ij} \) denotes the depth of the potential well. \( \sigma_{ij} \) for the atom pair \( i, j \) is calculated from the individual LJ size parameter of individual atoms \( \sigma_i \) and \( \sigma_j \) using a sixth power rule as shown in Eq. (A17), i.e.,

\[
\sigma_{ij} = \left[ \frac{1}{2} \left( \sigma_i^6 + \sigma_j^6 \right) \right]^{\frac{1}{6}},
\]

(A16)

To save computational time, both the \( \text{van der Waals} \) and Coulombic interactions are truncated after a cutoff distance \( r_c \), i.e., the potential is set to zero when the interatomic distance is larger than \( r_c \). For all simulations, a cutoff distance of 10 Å is used for both the \( \text{van der Waals} \) and the Coulombic interactions.

\( E_{\text{dihedral}} = \sum_{\phi} k_1 (1 - \cos(\phi)) + k_2 (1 - \cos(2\phi)) + k_3 (1 - \cos(3\phi)), \)

(A4)

\[ E_{\text{out-of-plane}} = \sum_{\chi} K \chi^2, \]

(A5)

\[ E_{\text{cross-coupling-term}} = E_{\text{bond-bond}} + E_{\text{bond-angle}} \]

\[ + E_{\text{bond-torsion}} + E_{\text{angle-angle}} \]

\[ + E_{\text{angle-torsion}} + E_{\text{angle-torsion}}. \]

(A6)

\[ E_{\text{bond-bond}} = \sum_{l,l'} h(l - l_0)(l' - l'_0), \]

(A7)

\[ E_{\text{bond-angle}} = \sum_{l,\theta} h'(l - l_0)(\theta - \theta_0), \]

(A8)

\[ E_{\text{bond-torsion}} = \sum_{l,\phi} (l - l_0)(g_1 \cos \phi + g_2 \cos 2\phi + g_3 \cos 3\phi), \]

(A9)

\[ E_{\text{angle-torsion}} = \sum_{\theta,\phi} (\theta - ed\theta_0)(g_1' \cos \phi \]

\[ + g_2' \cos 2\phi + g_3' \cos 3\phi), \]

(A10)

\[ E_{\text{angle-torsion}} = \sum_{\theta,\theta',\phi} k_{\text{aa}} (\theta - \theta_0)(\theta' - \theta'_0) \cos \phi, \]

(A11)

\[ E_{\text{angle-angle}} = \sum_{l,\theta} s(\theta - \theta_0)(\theta' - \theta'_0), \]

(A12)

\[ E_{\text{nonbonded}} = E_{\text{Coulomb}} + E_{\text{vdw}}, \]

(A13)

\[ E_{\text{Coulomb}} = \sum_{i,j} \frac{q_i q_j}{r_{ij}}, \]

(A14)

\[ E_{\text{vdw}} = \sum_{i,j} \epsilon_{ij} \left[ \frac{2 \alpha_{ij}}{r_{ij}} \right]^9 - 3 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6. \]

(A15)

Here, \( E_{\text{bond}} \) is the energy associated with change in bond length \( l \) during the simulation from equilibrium bond length \( l_0 \), and \( c_1, c_2, \) and \( c_3 \) denote the force constants associated with the bond stretching. The 3rd- and 4th-order terms in Eq. (A1) are considered along with the 2nd-order harmonic term in order to account for the anharmonic interactions in these polymers. \( E_{\text{angle}} \) denotes the energy associated with change in bond angle \( \theta \) from the equilibrium bond angle \( \theta_0 \) with \( d_1, d_2, \) and \( d_3 \) as associated force constants. The torsional potential energy \( E_{\text{dihedral}} \) is characterized by the change in the dihedral angle \( \phi \) from the equilibrium dihedral angles \( \phi_0 \) (\( \phi_0 = 0 \) for the present case) with \( k_1, k_2, \) and \( k_3 \) as associated force constants. The out of plane deformation is characterized by the out of plane angle \( \chi \) and the associated constant \( K \) as shown in Eq. (A5). The cross coupling terms account for the effect of one deformation on the other, e.g., the influence of bond stretching on angle bending. These are calculated from Eqs. (A7)–(A12). In these relations, \( \theta_0, f_0, \theta_0, g_1, g_2, g_3, g_1, g_2, g_3, h, h', \) and \( k_{\text{aa}} \) are all constants. The nonbonded interactions are given by \( E_{\text{nonbonded}} \) which is the sum of contributions from Coulombic \( (E_{\text{Coulomb}}) \) and \( \text{van der Waals} (E_{\text{vdw}}) \) interactions. For Coulombic interactions, as shown in Eq. (A14), \( q_i \) and \( q_j \) represent the partial charges of atoms separated by an interatomic distance of \( r_{ij} \). For calculating long range Coulombic interactions, a particle-particle particle-mesh\(^{16}\) algorithm is used. The \( \text{van der Waals} \) interactions are calculated in the form of a 6-9 Lennard-Jones (LJ) potential, as shown in Eq. (A16). Here, the size parameter \( \sigma_{ij} \) is the radial distance \( r_{ij} \) between the centers of atoms \( i \) and \( j \) at which the potential is zero and \( \epsilon_{ij} \) denotes the depth of the potential well. \( \sigma_{ij} \) for the atom pair \( i, j \) is calculated from the individual LJ size parameter of individual atoms \( \sigma_i \) and \( \sigma_j \) using a sixth power rule as shown in Eq. (A17), whereas the energy parameter \( \epsilon_{ij} \) for the atom pair \( i, j \) is given by the formula shown in Eq. (A17), i.e.,

\[
\sigma_{ij} = \left[ \frac{1}{2} \left( \sigma_i^6 + \sigma_j^6 \right) \right]^{\frac{1}{6}},
\]

(A16)

\[ \epsilon_{ij} = 2 \sqrt{\epsilon_i \epsilon_j} \sigma_{ij}^2 \sigma_{ij}^3 \sigma_{ij} \sigma_{ij}^6. \]

(A17)
25 See supplementary material at http://dx.doi.org/10.1063/1.3678848 for details of all the necessary force field parameters used to calculate the total potential energy of the system as described in the Appendix.