Molecular Origins of Polymer-Coupled Helical Motion of Ions in Crystalline PEO$_3$:NaI

6.1 Introduction

Solid polymer electrolytes (SPEs) are novel solid-state ion transporters with desirable electrochemical stability and mechanical flexibility. SPEs find their applications in solid state electrochemical devices such as thin-film batteries, electro-chromic devices, fuel cells, smart windows and clean energy storage devices. The mechanism of ion conduction in SPEs is believed to be complex and the atomic level understanding of which remains elusive. Unlike non-polymeric crystalline electrolytes in which ion transport occurs through rigid host framework, the flexibility of the polymer host is the key driving force for ion dynamics in SPEs. Although solid-state NMR line shapes and polymer relaxation rates measured for various SPEs continue to provide evidences for the coupling between polymer dynamics and ion transport in these novel materials, the molecular basis for the correlation between the polymer and ion dynamics is not well understood.\textsuperscript{7–10}

In the work presented in this chapter, we have used all-atom MD simulation and the adaptive biasing force (ABF) method to characterize the energetics of ion transport and coupling between polymer dynamics and ion conduction in a perfect and a defected crystalline PEO$_3$:NaI. In particular, the free energy profiles and activation energies for the cation and anion transport along the polymer tunnel, and crucial factors determining the free energy
barriers are examined. The defect-induced structural variations and changes in the conformational flexibility of PEO are also investigated. The results reveal distinct helical ion transport pathways mirroring the helical symmetry of the polymer indicating a unique conduction mechanism in crystalline PEO$_3$:NaI.

6.2 Simulation details

6.2.1 Model systems

The MD simulations were performed on two crystalline PEO$_3$:NaI models: Model-I (Figure 6.1(c)) represents the ideal PEO$_3$:NaI crystal with no point defects and Model-II is a defected crystal with a chosen nearest-neighbor Na$^+$-I$^-$ pair removed from the lattice sites (Figure 6.1(d)). The experimental crystal structure of PEO$_3$:NaI was used as the starting structure for the MD simulation of Model-I (Figure 6.1(a) and 6.1(b)).$^{109}$ The simulated $2 \times 4 \times 8$ crystal consisted of 64 unit cells (2, 4 and 8 unit cells along the $\vec{a}$, $\vec{b}$ and $\vec{c}$ axes, respectively) with 16 PEO chains, each having 28 monomers and methyl end-caps with a molecular formula $CH_3O - (C_2H_4O)_{28} - CH_3$ (MW=1.278 kDa), oriented parallel to the fiber axis of the crystal.$^{109}$ The starting structure of Model-II was identical to that of Model-I except for the missing nearest-neighbor Na$^+$-I$^-$ ion pair. Model-I provides insights into the nature of fluctuations of ions and polymer chains around their equilibrium positions while Model-II is used to probe the mechanism and energetics of defect-induced ion hopping and the coupling between polymer dynamics and ion transport in the crystalline PEO$_3$:NaI.

6.2.2 MD details

The all-atom MD simulations were carried out in the isothermal-isobaric ensemble using LAMMPS with the force field parameters taken from the work of Neyertz et al.$^{123-125}$ The anisotropic pressure control was achieved using the Parrinello-Rahman method with a time constant of 1 ps and the temperature was controlled using the Nosé-Hoover chain thermostats with a time constant of 0.1 ps.$^{176,177,216}$ Three dimensional periodic boundary conditions consistent with the symmetry of the unit cell were applied. The long-range electrostatic in-
Figure 6.1: A schematic representation of the structure of PEO$_3$:NaI crystal with 64 unit cells (2×4×8 system) (a) view perpendicular to the chain axis and (b) view along the chain axis. The polymer chain that wraps around the cation vacancy (labelled as Na$_2$) and anion vacancy (labelled as I$_3$) in the (c) undefected (Model-I) and (d) defected (Model-II) models of 2×4×8 PEO$_3$:NaI crystal is shown together with the coordinated ions. The carbons (green), oxygens (red), Na$^+$ (blue) and I$^-$ (purple) are shown. Hydrogens are not shown for clarity.
6.2. Simulation details

Interactions were treated using the particle-particle particle-mesh Ewald (PPPM) method with a real space cut-off of 12 Å. The systems were subjected to energy minimization using the conjugate gradient method followed by 5 ns equilibration and 50 ns production runs in the NPT ensemble at 300 K and 1 atm pressure with a time step of 1 fs.

6.2.3 Adiabatic calculations

The potential energy of a cation at every point along its diffusion pathway between adjacent cation sites in PEO₃:NaI crystalline environment is described by the adiabatic potential energy profile. By decomposing the adiabatic energy profiles into components arising out of different types of interactions, the contributions of critical interactions to the stability of the cations in their crystallographic positions and to energy barriers for cation diffusion in PEO₃:NaI systems can be understood. The adiabatic energy profiles are obtained by displacing a cation of interest in discrete incremental steps from its crystallographic position to the adjacent cation site along the most-probable transport pathway while keeping the remaining atoms restrained at their respective crystallographic positions. The adiabatic decoupling of the mobile cation from the frozen environment enables us to get partial information about the enthalpic contributions to cation transport in PEO₃:NaI crystals.

At any point along the chosen pathway, the cation of interest interacts with other Na⁺, I⁻, C_{PEO}, H_{PEO}, and O_{PEO} atoms. The electrostatic and van der Waals energies of the tagged cation of interest with a given type of surrounding atom can be calculated and plotted as a function of a suitable reaction coordinate that describes the cation transport between adjacent sites along the chosen path. In the present study, three successive Na⁺ ions (labelled as Na₁, Na₂, and Na₃) in Figure 6.2 were chosen and the distance between Na₁ and Na₃ (D₁₃) was used as a reaction coordinate of interest. Na₃ was displaced from its crystallographic position along Na₂-Na₁ and Na₂-Na₃ bond vectors in incremental steps of 0.01 Å to generate around 70 configurations of PEO₃:NaI crystal that differ only in the position of Na₃. The potential energies of the system and Na₃ were calculated for all these configurations and plotted as a function of D₁₃. A schematic representation of the chosen Na⁺ ions and the instantaneous positions of Na₃ in different configurations (blue spheres) for Model-I are shown in Figure
6.3. Results and discussion

We emphasize here that the key molecular events such as ion hopping and conformational changes in PEO were observed during the first 10 ns of a 50 ns-long MD trajectory. In what follows, the results obtained from the first 10 ns segment of the MD trajectory are only presented for clarity.

6.3.1 Validation of models

In polymer crystal simulations, a standard procedure to validate the simulated models is to compare the computed lattice parameters, radial distribution functions (RDFs), and the polymer dihedral distributions against the corresponding experimental data obtained from the
crystal structures. The experimental comparison of each of the above mentioned quantities for the simulated PEO$_3$:NaI crystals are compared individually in the following subsections. At the beginning of each subsection, the MD-derived quantity of interest for Model-I (perfect crystal) is compared with the corresponding experimental data to examine how close the simulated crystal is from the X-ray resolved crystal structure. Subsequently, the data for the defected crystalline model (Model-II) are compared with those for Model-I to quantify the defect-induced changes in these properties. In addition to the comparison of the MD-derived average values and distributions of quantities of interest against experimental data, the time evolution of these quantities obtained from MD simulations can also be used to validate the models. For instance, a significant drift or a large deviations (or fluctuations) of these quantities around their respective average values may correspond to unstable or unrealistic simulations.

### 6.3.2 Lattice parameters

The time evolution of the MD-derived lattice parameters for two different simulated models of PEO$_3$:NaI is shown in Figure 6.3. Table 6.1 compares the calculated lattice parameters against the experimental data. It is evident from the time evolution that the lattice parameters do not drift with time but exhibit smaller fluctuations (with a standard deviation range of 0.01-0.09Å for the cell lengths and 0.12-0.15° for the cell angles) around the expected average values tabulated in Table 6.1. The calculated lattice parameters for Model-I agree reasonably well with the experimental data suggesting that the force field parameters used in the present study realistically stabilize the expected PEO$_3$:NaI crystalline state. A marginal difference of ~0.3Å and ~1° observed between the calculated and experimental $b$ and $\gamma$ lattice parameters, respectively, can be attributed to the end-effects exhibited by CH$_3$ end capped finite polymer chains in the simulated crystalline models. To probe the response of the lattice parameters to Na$^+$/I$^-$ point defects, the calculated lattice parameters of the defected crystals are compared with those computed for Model-I. The lattice parameters of the defected crystals are almost equal to those for the pristine crystal indicating that removal of a cation and an anion (the formation of a pair of point defects) does not alter the overall lattice structure of the crystalline
Table 6.1: The time-averaged unit cell parameters and polymer dihedral angles obtained from 10 ns MD simulations performed at 300K and at 1 atm pressure for different PEO$_3$:NaI crystalline models studied here are compared against the corresponding experimental values.$^{218}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model-I</th>
<th>Model-II</th>
<th>Experimental$^{218}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>18.09 ± 0.09</td>
<td>18.14 ± 0.06</td>
<td>18.15</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.76 ± 0.03</td>
<td>8.74 ± 0.02</td>
<td>8.41</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.95 ± 0.01</td>
<td>7.94 ± 0.01</td>
<td>7.98</td>
</tr>
<tr>
<td>α (deg)</td>
<td>90.80 ± 0.12</td>
<td>90.48 ± 0.13</td>
<td>90.0</td>
</tr>
<tr>
<td>β (deg)</td>
<td>90.33 ± 0.13</td>
<td>90.25 ± 0.13</td>
<td>90.0</td>
</tr>
<tr>
<td>γ (deg)</td>
<td>123.23 ± 0.14</td>
<td>123.14 ± 0.13</td>
<td>122.3</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>1053.04 ± 2.54</td>
<td>1054.19 ± 2.47</td>
<td>1029.6</td>
</tr>
<tr>
<td>$CC_g$ s(deg)</td>
<td>299.84 ± 4.9</td>
<td>299.9 ± 4.89</td>
<td>293.1</td>
</tr>
<tr>
<td>$CC_g^-$ (deg)</td>
<td>60.12 ± 4.9</td>
<td>60.19 ± 4.89</td>
<td>62.3</td>
</tr>
<tr>
<td>CO (deg)</td>
<td>180 ± 7.7</td>
<td>179.97 ± 7.67</td>
<td>180.6</td>
</tr>
</tbody>
</table>

PEO$_3$:NaI.

### 6.3.3 Dihedral distributions

Since polymer conformation plays an important role in the conduction of ions in SPEs, it is essential to examine how well the conformational properties of PEO in the simulated PEO$_3$:NaI crystals compare with experimental results. The backbone dihedral angle distributions of PEO are used for this purpose. The dihedrals around the C-C (O-C-C-O quadruplets) and C-O (C-C-O-C and C-O-C-C quadruplets) bonds are the two types of backbone dihedrals present in PEO. Figure 6.4 compares the C-O and C-C backbone dihedral distributions of the simulated PEO$_3$:NaI crystals with the experimental data. The crystal structure of PEO$_3$:NaI resolved using X-ray diffraction reveals that the C-C-O-C-C-O-C-C-O segments of PEO follow a $ttgttgtg^-$ conformational sequence giving rise to a helical conformation to accommodate
the cations inside the helices. That is, all the C-O dihedrals exist only in the \( t \) conformational state while the C-C dihedrals equally populate the \( g^- \) and \( g \) conformational states with zero population in the \( t \) state. These are evident from the distributions of \( \phi_{C-O} \) and \( \phi_{C-C} \) obtained from the experimental crystal structure shown in Figure 6.4. Both the experimental and MD-derived \( P(\phi_{C-O}) \) for Model-I show a unimodal distribution centered around \( \phi_{C-O} \sim 180^\circ \). However, the MD-derived \( P(\phi_{C-O}) \) is relatively broader than that obtained from the static crystal structure due to thermal motions of the atoms about their equilibrium positions during MD simulations. As for the C-C dihedral distributions, both the experimental and MD-derived \( P(\phi_{C-C}) \) for Model-I exhibit bimodal distributions with two peaks at \( \phi_{C-C} \sim 60^\circ \) and \( \phi_{C-C} \sim 300^\circ \) corresponding to the \( g^- \) and \( g \) states, respectively. The average values around C-C and C-O torsions of PEO oligomer in PEO\({}_3\):NaI are shown in Table 6.1. These observations indicate the overall conformational properties of PEO in Model-I are consistent with the experimental results.

In order to quantify the salt-induced and defect-induced changes in the conformation of PEO in PEO\({}_3\):NaI crystals, the backbone dihedral distributions of the perfect PEO\({}_3\):NaI crystal is compared with the pristine PEO crystal and the defected PEO\({}_3\):NaI crystals, respectively. A comparison of the polymer dihedral distributions in PEO and PEO\({}_3\):NaI crystals sheds light on salt-induced conformational changes in PEO brought about by the complexation of \( \text{Na}^+ \) ions with the \( \text{O}_{PEO} \) atoms while a similar comparison between Model-I and Model-II provides information on defect-induced changes in PEO conformation. We first compare experimental dihedral distributions obtained from the static crystal structures of PEO and PEO\({}_3\):NaI. In the PEO crystal, the C-O dihedral angles are widely distributed with a mean of \( \phi \sim 187^\circ \) and a standard deviation of \( \sim 8^\circ \) giving rise to a distorted helical conformation of PEO. The distortion from a perfect helical conformation was attributed to the strong intermolecular interactions between PEO chains in the crystal but MD simulations have questioned about it. The corresponding distribution in the PEO\({}_3\):NaI crystal is sharply peaked around \( \phi \sim 180^\circ \) with a mean of \( \phi \sim 180.6^\circ \) and a standard deviation of \( \sim 8^\circ \) leading to an ordered helical conformation of PEO. The salt-induced narrowing of dihedral distributions resulting in a disordered to ordered helical conformation and changes in the PEO helical pitch underscores the complex
Figure 6.4: The backbone dihedral distributions of PEO obtained from MD simulations of different models of PEO$_2$:NaI crystal: Model-I (blue) and Model-II (magenta). The corresponding dihedral distributions obtained from the experimental crystal structures of PEO$_2$:NaI (red) and PEO (black) are also shown. (a) C-O dihedral distributions; (b) C-C dihedral distributions around the $g^-$ conformational state; (c) C-C dihedral distributions around the $g$ conformational state. PEO crystal MD data is shown in green colour.
interplay between the stability of ions and polymer conformation. However, the MD-derived C-O dihedral angle distributions of crystalline PEO and PEO\textsubscript{3}:NaI overlap completely suggesting that thermal fluctuations of atom about their equilibrium positions are similar in both crystals (pristine PEO and PEO\textsubscript{3}:NaI) and the inability of force field parameters to capture the conformation changes in the PEO oligomer while going from pristine PEO crystals to PEO\textsubscript{3}:NaI crystals.

The overall conformational distributions of PEO in the defected PEO\textsubscript{3}:NaI crystal (Model-II) are compared with those in the perfect crystal (Model-I) in Figure 6.4. The similarity of the C-O dihedral angle distributions for all the simulated crystals suggests that the overall conformational distribution of PEO is unchanged by the presence of a single point defect or an ion-pair defect in the crystalline SPE. The calculated C-C dihedral distributions (panels (b) and (c) in Figure 6.4) for all the simulated PEO\textsubscript{3}:NaI crystals exhibit two peaks of equal intensity at $\phi \sim 60^o$ and $\phi \sim 300^o$ corresponding to the gauche- ($g^-$) and gauche ($g$) conformational states, respectively.

### 6.3.4 Radial distribution functions

The radial distribution functions (RDF) provide detailed insights into the structural arrangement and the distribution of atoms around any given central atom. Figure 6.5 compares the MD-derived RDFs for different pairs of atoms in the simulated crystals with the corresponding experimental RDFs obtained from the crystal structure. The following naming convention is used in this chapter to denote different RDFs computed for PEO\textsubscript{3}-NaI crystals: $g_{X-Y}^J(r)$ denotes the RDF quantifying the radial distribution of Y-type atoms around a central X-type atom in the $J^{th}$ crystalline model of PEO\textsubscript{3}-NaI, $r$ denotes the distance between atoms X and Y and the values of $J$ can be I (Model-I), II (Model-II), and $J=\text{EXP}$ represents the corresponding RDF computed from the experimental crystal structure. $g_{\text{Na-O}}^{\text{EXP}}(r)$ (Figure 6.5(a)) consists of three sharp peaks at 2.23 Å, 2.58 Å, and 3.30 Å in the first coordination shell ($r < 3.6$ Å) with 4 NN O\textsubscript{PEO} coordinated to each Na\textsuperscript{+} ion. The first two peaks in $g_{\text{Na-O}}^{\text{EXP}}(r)$ arises from the three proximal ($r \sim 2.45$ Å) NN O\textsubscript{PEO} atoms while the remaining NN O\textsubscript{PEO} atom is slightly far ($r \sim 3.32$ Å) from the central Na\textsuperscript{+} ion and contributes to the third peak. The MD-derived
$g_{Na-O}^f(r)$ shows that the first coordination shell consists of an intense first peak at $r \sim 2.52$ Å with a shoulder at $r \sim 2.82$ Å followed by a minimum at $r \sim 3.60$ Å. The coordination number at the first minimum (at $r=3.60$ Å) is 4. The second coordination shell extends from $r \sim 3.61$ Å to $r \sim 5.13$ Å with a peak at $r \sim 4.44$ Å arising from two second-shell O$_{PEO}$ atoms each coordinated to the adjacent Na$^+$ ions on either side of the central Na$^+$ along the polymer chain axis. The peaks in the calculated RDFs are broader than those observed in static structure-based $g_{Na-O}^{EXP}(r)$ due to the thermal fluctuations of atoms in the MD simulation. The coordination shell structure and distance-dependent distributions of O$_{PEO}$ atoms around cations inferred from the calculated $g_{Na-O}^f(r)$ for the perfect PEO$_3$:NaI crystal are consistent with the experimental results. The calculated Na-O RDFs for the defected crystals are almost identical to that obtained for the perfect crystal suggesting that the overall distribution of O$_{PEO}$ atoms around Na$^+$ ions are not altered by a pair of point defects in the crystalline PEO$_3$:NaI.

$g_{Na-C}^{EXP}(r)$ exhibits multiple peaks at shorter distances ($3 \text{ Å} < r < 4.5 \text{ Å}$) with a coordination number of $\sim 10$ at $r=4.98$ Å. A pair of C$_{PEO}$ atoms covalently bonded to each of the four NN O$_{PEO}$ coordinated to a given Na$^+$ ion contribute to eight C$_{PEO}$ atoms in the first coordination shell while each of the remaining two C$_{PEO}$ is bonded to the O$_{PEO}$ located at the interface between the first and second coordination shells of the central Na$^+$ ion. $g_{Na-C}^f(r)$ shows a peak at 3.42 Å followed by a minimum at 4.60 Å with a coordination number of 10 at $r=4.52$ Å. The consistency between the calculated and experimental coordination numbers of the first coordination shell suggests that all the sub-peaks observed at $r < 4.5$ Å in $g_{Na-C}^{EXP}(r)$ are merged into a single peak in $g_{Na-C}^f(r)$ due to thermal fluctuations of atoms about their crystallographic positions. A relatively broad second coordination shell ($4.61 \text{ Å} < r < 8.0 \text{ Å}$) has a hump at 5.38 Å and a broad peak at 6.58 Å. Both the C$_{PEO}$ atoms of the polymer chain coordinated to the central Na$^+$ ion (referred to here as intra-chain C$_{PEO}$ atoms) and from the neighboring chains (referred to here as inter-chain C$_{PEO}$ atoms) contribute to the second coordination shell. The first coordination shell for all the simulated crystals are identical suggesting that the overall distribution of C$_{PEO}$ atoms around Na$^+$ ions is invariant to a pair of point defects creation in the crystalline PEO$_3$:NaI. The second coordination shell in Model-
Figure 6.5: Radial distribution functions (solid lines) and running coordination numbers (dashed lines) in Model-I (red), Model-II (green), and the experimental crystal structure (black). (a) Na-O (b) Na-C (c) Na-I (d) Na-Na (e) I-C (f) I-O.
Figure 6.6: Radial distribution functions (solid lines) and running coordination numbers (dashed lines) in Model-I (red), Model-II (green), and the experimental crystal structure (black). (d) O-O (e) C-C (f) C-O and the corresponding intra-molecular distributions (a) O-O (b) C-C (c) C-O.

The experimental $g_{\text{Na-I}}^{\text{EXP}}(r)$ shows two peaks at around $r = 3.12$ Å with a coordination number of 2 indicating that each Na$^+$ ion in the perfect crystal is coordinated by two NN I$^-$ ions with $r_{\text{Na-I}} < 3.12$ Å. The MD-derived $g_{\text{Na-I}}^I(r)$ shows a single peak at 2.52 Å with a coordination number of 2 at $r = 2.85$ Å. The sub-peaks observed at $r < 3.6$ Å in $g_{\text{Na-I}}^{\text{EXP}}(r)$ merged into a single peak in $g_{\text{Na-I}}^I(r)$ due to the thermal fluctuations of atoms about their crystallographic positions. The second coordination shell ($5.5 < r < 6.8$ Å) has the contributions from both the intra-chain (iodides within the helix of the coordinated polymer) and inter-chain (iodides in the helices of neighbouring chains) iodides. The overall peak positions in $g_{\text{Na-I}}^I(r)$ shifted to lower $r$ values by 0.5 Å when compared to the peak positions in
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\( g^{\text{EXP}}_{\text{Na}^-\text{I}^-}(r) \). Shifting of peak positions to lower \( r \) values can be attributed to the over estimation of the Na\(^+\)-I\(^-\) interactions in crystalline PEO\(_3\):NaI by the force-field parameters.

\( g^{\text{EXP}}_{\text{Na}-\text{Na}}(r) \) exhibits a single peak at \( r = 4.26 \text{ Å} \) with a coordination number of 2 indicating that each Na\(^+\) ion in the undefected PEO\(_3\):NaI crystal is coordinated by two equispaced NN Na\(^+\) ions. The second coordination shell (\( 7 \text{ Å} < r < 10 \text{ Å} \)) exhibits multiple peaks arising from both the intra-chain (sodium ions present in the same helix) and inter-chain (sodium ions present in the neighbouring helices) sodium ions. The MD-derived \( g^{I}_{\text{Na}-\text{Na}}(r) \) is consistent with the \( g^{\text{EXP}}_{\text{Na}-\text{Na}}(r) \) with a peak positioned at \( r = 4.08 \text{ Å} \). All the essential features in the second coordination shell of \( g^{\text{EXP}}_{\text{Na}-\text{Na}}(r) \) are captured in the MD-derived \( g^{I}_{\text{Na}-\text{Na}}(r) \) and merging of the peaks in the second shell is due to the thermal fluctuations of ions around their equilibrium positions.

\( g^{\text{EXP}}_{\text{I}-\text{C}}(r) \) also exhibits multiple peaks at shorter distances \( r < 5.5 \text{ Å} \) with a coordination number of \( \sim 22 \) at \( r = 5.4 \text{ Å} \). Both the intra-chain and inter-chain C\(_{\text{PEO}}\) atoms contribute to the peaks at \( r < 5.5 \text{ Å} \). Multiple peaks observed in \( g^{\text{EXP}}_{\text{I}-\text{C}}(r) \) at \( r < 5.5 \text{ Å} \) merged into a single peak positioned at 4.45 Å in MD-derived \( g^{I}_{\text{I}-\text{C}}(r) \). The MD-derived I-C RDFs for the defected crystals are almost identical to that obtained for the perfect crystal.

\( g^{\text{EXP}}_{\text{I}-\text{O}}(r) \) also exhibits multiple peaks at distances \( r < 4.45 \text{ Å} \) with a coordination number of \( \sim 7 \) at \( r = 4.50 \text{ Å} \). The peaks at \( r < 4.3 \text{ Å} \) are due to intra-chain O\(_{\text{PEO}}\) atoms whereas peak at \( r > 4.3 \text{ Å} \) have contributions from both intra- and inter-chain O\(_{\text{PEO}}\) atoms. The MD-derived \( g^{I}_{\text{I}-\text{O}}(r) \) shows a single peak at 3.80 Å obtained by merging of peaks at distances \( r < 4.45 \text{ Å} \) in \( g^{\text{EXP}}_{\text{I}-\text{O}}(r) \). I-O RDFs for the defected PEO\(_3\):NaI crystals are almost identical to that obtained for the perfect crystal.

The radial distribution functions (RDF) involving only polymer atoms (i.e., O\(_{\text{PEO}}\) and C\(_{\text{PEO}}\)) are shown in Figure 6.6. The corresponding intra-molecular radial distributions (RDFs calculated by considering only atoms with in the single PEO chain) are also shown (Figure 6.6(a), 6.6(b) and 6.6(c)). The MD-derived radial distributions are consistent with the with the experimental results. The calculated RDFs for the defected crystals are almost identical to that obtained for the perfect crystal suggesting that the overall conformation of the polymer is not altered by a pair of point defects in the crystalline PEO\(_3\):NaI.
The detailed analyses based on RDFs reveal that there is a marginal difference between the some of the calculated and experimental RDFs. This inconsistency indicate that there is room for improvement of the force field parameters used in our simulation. In particular, the current force field parameters overestimate the Na-I affinity and a slight decrease in the Na-I affinity is likely to provide better estimates of the MD-derived RDFs.

6.3.5 Ion transport pathways

The MD-derived diffusion paths of the cations and anions in Model-II (Figures 6.7(a) and 6.7(b)) reveal that the anions follow a helical pathway mirroring the helical symmetry of the polymer. The anion helical path and the PEO helix are intertwined to form a double helix-like column facilitating the cation transport within it. Although the helical paths of ions and the PEO helix have a common helical axis, the radii of these helices differ significantly; the radius of the PEO helix is the largest while that of the cation helical path is the smallest. To understand the molecular basis for helical transport of ions and to elucidate the mechanism of ion hopping and associated structural and energetic changes in Model-II, the time evolution of $D_{13}$, $D_{24}$, van der Waals and electrostatic energies of ions proximal to the void (Na$_1$, Na$_3$, I$_2$, and I$_4$ in Figure 6.1(d)) was examined. In the perfect crystal $D_{13}$ and $D_{24}$ fluctuate around their mean values of $7.85 \pm 0.20\text{Å}$ and $7.86 \pm 0.22\text{Å}$, respectively (Figure 6.8), which are in reasonable agreement with earlier MD and experimental results.\(^{109,124}\) In Model-II, however, $D_{13}$ fluctuates around three different values (4.02Å, 5.0Å, and 7.0Å) and exhibits abrupt transitions between them at different time intervals (Figure 6.9(a)). For $t \leq 3.7$ ns, $D_{13}$ fluctuates around 5.0Å followed by an abrupt increase to 7.0Å at $\sim 3.7$ ns. $D_{13}$ fluctuates around 7.0Å for $3.7 \text{ ns} \leq t \leq 5.0$ ns and jumps from 7.0Å to 5.0Å and from 5.0Å to 4.02Å at $t \sim 5$ ns and $t \sim 6.8$ ns, respectively. Similarly, $D_{24}$ also exhibits transitions between three different values (5.13Å, 5.37Å, and 7.66Å) precisely at times coinciding with the $D_{13}$ transitions (Figure 6.9(e)).

A closer examination of the time evolution of the displacements of Na$_1$ and Na$_3$ from their initial positions reveals that the abrupt changes in $D_{13}$ are due to the hopping of Na$_3$ between its lattice position and the vacancy site. Na$_1$ remained in its lattice position during
Figure 6.7: The MD-derived diffusion pathways of the (a) cations and (b) anions in Model-II. The entire crystal is not shown for clarity. The polymer chain that wraps around the cation vacancy (labelled as Na$_2$) and anion vacancy (labelled as I$_3$) is only shown. The carbons (green), oxygens (red), Na$^+$ (blue) and I$^-$ (purple) are also shown. Hydrogens are not shown for clarity. The crystallographic positions of different (a) Na$^+$ (small spheres of different colors) (b) I$^-$ (large spheres of different colors) and their corresponding instantaneous positions (points) during MD simulations are shown with (a) I$^-$ (purple) and (b) Na$^+$ (blue) counter ions. The ellipses denote the location of the vacancy in the initial structure. The fluctuations of the polymer atoms are not shown for clarity.
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Figure 6.8: Time evolution of (a) $D_{13}$, (b) $D_{24}$, (c) helical pitch ($P_h$), and (d) radius of gyration ($R_g$) of PEO in Model-I.

Figure 6.9: Time evolution of (a) $D_{13}$ (e) $D_{24}$ (d) the helical pitch ($P_h$) of PEO$_D$ (h) the radius of gyration ($R_g$) of PEO$_D$ and the van der Waals (red) and electrostatic (black) potential energies of (b) Na$_1$ (c) Na$_3$ (f) I$_2$ and (g) I$_4$ in Model-II.
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Figure 6.10: Time evolution of the displacement of Na$_1$ (black) and Na$_3$ (red) from their initial positions in Model-II obtained during the equilibration phase of the MD simulation performed at 300K.

The synchrony between the transitions in D$_{13}$ and D$_{24}$ reveals a strong correlation between the cation and anion hopping in the crystalline PEO$_3$:NaI. The abrupt changes in the electrostatic energies of Na$_3$ and the anions proximal to the void (Figure 6.9(c,f,g)) coincide with transitions in D$_{13}$ and D$_{24}$ indicating that the defect-induced electrostatic imbalance near the void is the underlying driving force for the ion hopping in Model-II. The molecular basis for the observed helical transport of ions in Model-II derived from these observations is that upon removal of a Na$^+$-I$^-$ ion pair from the crystal, an electrostatic imbalance is created near the void leading to the displacement of ions surrounding the vacancy site. In particular, the Na$^+$ and I$^-$ (Na$_3$ and I$_2$ in Figure 6.1(d)) ions proximal to the vacancy exhibit large-amplitude displacements in response to the creation of void. Consequently, these proximal ions are likely to hop to the adjacent vacancy sites via an energy minimum helical path to optimize their electrostatic interactions with the surrounding atoms. A single ion hopping event near the vacancy results in a concerted hopping of other ions in the polymer tunnel leading to the displacement of the void to the ends of the polymer.
Figure 6.11: Ion conduction pathways in Model-II of crystalline PEO$_3$:NaI with different molecular weights (chain lengths).
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This unique concerted, collective hopping of ions is facilitated by tight molecular packing and the presence of long-range correlations in the crystal.

A movie obtained from the MD trajectory demonstrating the mechanism of ion hopping in Model-II is provided in Supporting Information. The MD trajectories obtained for $2 \times 4 \times 4$ and $2 \times 4 \times 16$ crystals reveal that the mechanism, pathway of ion transport and the associated conformational responses of PEO are almost insensitive to the chain length (Figure 6.11). The chain length dependence of the ionic conductivity and the diffusion coefficients of the ions could not be examined in our study due to a limited number of ion hopping events observed during 50 ns MD simulation (a free energy-based molecular basis for the absence of many hopping events is provided in the following section). However, earlier studies have demonstrated that the ionic conductivity and diffusion coefficients of ions in amorphous SPEs vary with the polymer chain length. The observed ion transport via well-defined helical pathways in crystalline PEO$_3$:NaI may be of more relevance to ordered crystalline SPEs at low temperatures around 300 K. However, several other transport mechanisms including ion jumps between polymer chains and ion motion together with the polymer chain may also contribute to ionic conductivity of disordered amorphous SPEs at elevated temperatures.

6.3.6 Free energy profiles for ion conduction

The ABF-derived free energy profiles provide a detailed insight into the energy barriers and relative stabilities of different ion sites along the helical ion transport pathways in the crystalline PEO$_3$:NaI. F(D$_{13}$) (Figure 6.12(a)) consists of three minima located at D$_{13}$=4.02Å, D$_{13}$=5.0Å and D$_{13}$=7.0Å and these minimum energy states are referred to here as the O-state, I-state, and D-state, respectively (O, I and D denote occupied, intermediate, and defected states, respectively). The positions of these minima are consistent with the three most probable values of D$_{13}$ observed in the MD-derived time evolution of D$_{13}$ (Figure 6.9(a)). The O-state is ~9.38 kcal/mol and ~10.85 kcal/mol more stable than the I- and D-states, respectively. The I-state is ~1.47 kcal/mol lower in energy than the D-state.

The structures corresponding to these minimum energy states are shown in Figure 6.12(c). In the D-state, Na$_1$ and Na$_3$ are separated by the vacancy while Na$_3$ occupies the vacancy site.
Figure 6.12: The ABF-derived free energy profiles for the (a) cation (F(D_{13})) and (b) anion (F(D_{24})) hopping and (c) accompanying structural changes in Model-II.
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Figure 6.13: Time evolution of D\textsubscript{13} in Model-II at different temperatures during the equilibration (black) and production (red) phases of the simulation.

in the O-state. In the I-state, the ions proximal to the vacancy (Na\textsubscript{1}, Na\textsubscript{3} and I\textsubscript{2} in Figure 6.1(d)) rearrange to form a linear Na-I-Na chain near the void while other Na-I-Na chains maintain the zig-zag pattern elsewhere. The effective activation barrier ($\Delta F_{\text{O} \rightarrow \text{D}}^C$) for cation hopping from the O-state to the D-state is $\sim 14.5$ kcal/mol while that from the O- and D-states to the I-state ($\Delta F_{\text{O} \rightarrow \text{I}}^C$ and $\Delta F_{\text{D} \rightarrow \text{I}}^C$) are $\sim 9.93$ kcal/mol and $\sim 3.15$ kcal/mol, respectively (Figure 6.12(a)). The energy penalty for a cation to hop from the I-state to the O- and D-states ($\Delta F_{\text{I} \rightarrow \text{O}}^C$ and $\Delta F_{\text{I} \rightarrow \text{D}}^C$) are $\sim 0.60$ kcal/mol and $\sim 4.60$ kcal/mol, respectively. F(D\textsubscript{24}) (Figure 6.12(b)) shows a deep minimum at D\textsubscript{24}=5.1 Å and a shallow minimum at D\textsubscript{24}=7.67 Å consistent with the time evolution of D\textsubscript{24} obtained from MD trajectories (Figure 6.9(e)). Both the I- and O-states contribute to the minimum in F(D\textsubscript{24}) observed at D\textsubscript{24}=5.1 Å while D\textsubscript{24}=7.67 Å in the D-state. The activation barrier ($\Delta F_{\text{I} \rightarrow \text{D}}^A$ and $\Delta F_{\text{O} \rightarrow \text{D}}^A$) for anion hopping from the I- and O-states to the D-state is $\sim 8.9$ kcal/mol while that for the reverse transition ($\Delta F_{\text{D} \rightarrow \text{I}}^A$ and $\Delta F_{\text{D} \rightarrow \text{O}}^A$) is 4.1 kcal/mol.

Since the activation barriers for the O→D transition are relatively higher than those for
the D→O transition, the transition probability, which is proportional to $e^{-\frac{\Delta F}{k_B T}}$, is relatively higher for the D→O transition than that for the O→D transition. Consequently, the D→O transition occurs only once (refer Figure 6.9) in the 50ns MD simulation and the system remains “trapped” in the O-state after the D→O transition. The O→D transition was absent even in the additional 10 ns MD simulations performed at higher temperatures staring from 350 K to 600 K in steps of 50 K (Figures 6.13 and 6.14).

The absence of multiple barrier crossings and prohibitively high barriers preventing the O→D transition suggest that it is practically impossible to determine accurately the activation barriers and the ionic conductivity from the 50ns MD trajectory. In the present study, the 50ns MD trajectory is used only to probe the migration pathways of ions and the conformational responses of PEO during the D→O transition. However, the MD trajectories obtained at different temperatures can be used to determine the curvatures of the free energy profiles associated with D_{13} and D_{24} at the most stable state of the system. It evident from F(D_{13}) and F(D_{24}) that the O-state is the most stable state of Model-II and the system resides in this
state for a longer period of time during the course of MD simulation. By considering only the portions of the MD trajectories in which the system stayed in the O-state, the temperature dependence of the magnitude of fluctuations in $D_{13}$ ($\langle (\Delta D_{13})^2 \rangle = \langle (D_{13} - \langle D_{13} \rangle)^2 \rangle$) and $D_{24}$ ($\langle (\Delta D_{24})^2 \rangle = \langle (D_{24} - \langle D_{24} \rangle)^2 \rangle$) in the O-state can be examined. $\langle \Delta D_{13}^2 \rangle$ increases linearly with temperature (Figure 6.15(a)) with a slope equal to $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the temperature. The harmonic well ($\frac{1}{2} K (D_{13} - \langle D_{13} \rangle)^2$) constructed from the MD-derived $K$ value fits very well with the harmonic portion of $F(D_{13})$ around the O-state (Figure 6.15(a)). Similarly, the harmonic well obtained from the fluctuations of $D_{24}$ also reproduces the harmonic portion of $F(D_{24})$ around the O-state (Figures 6.15(b) and 6.16(b)).

6.3.7 Adiabatic energies

The $Na_3$-$O_{PEO}$ interaction energy profiles (the total potential energy, vdW, and electrostatic energies) for different models are shown in Figure 6.17(a). In Model-I, the total $Na_3$-$O_{PEO}$ potential energy profile shows minima at $D_{13}=4.0 \text{ Å}$ and $D_{13}=8.3 \text{ Å}$ separated by a barrier of 15 kcal/mol at $D_{13}=6.0 \text{ Å}$. The presence of two minima indicate that there are two energetically favourable coordination environments provided by the $O_{PEO}$ atoms possible for the cation of interest along its transport pathway and the locations of these minima with $D_{13}=4.0$...
Figure 6.16: Comparison of ABF-derived free energy profiles (black) with the MD-derived harmonic wells (red) obtained from the temperature dependence of $<\Delta D_{13}^2>$ and $<\Delta D_{24}^2>$.

$D_{13}=8.3$ Å and $D_{13}=6.0$ Å correspond to the crystallographic positions of Na$_2$ and Na$_3$, respectively. At the first minimum at $D_{13}=4.0$ Å Na$_3$ is coordinated to four O$_{PEO}$ atoms with the minimum and maximum Na$_3$-O$_{PEO}$ NN distances being 2.22 Å and 3.3 Å, respectively. However, at the barrier (at $D_{13}=6.0$ Å) Na$_3$ is coordinated by three O$_{PEO}$ atoms with the minimum and maximum Na$_3$-O$_{PEO}$ NN distances being 1.95 Å and 2.93 Å, respectively. The decrease in the coordination number and Na$_3$-O$_{PEO}$ distances are the critical factors contributing to the energy barrier at $D_{13}=6.0$ Å. Two coordinating O$_{PEO}$ atoms are commonly present in both the energy minimum and barrier configurations whereas the one of remaining two NN O$_{PEO}$ atoms in the minimum energy configuration is replaced by another O$_{PEO}$ atoms while the other NN O$_{PEO}$ moves out of the first coordination shell of the mobile cation in the barrier configuration. The dihedrals involving these displaced NN O$_{PEO}$ atoms are expected to play a vital role in the transport of cations in PEO$_3$:NaI.

The potential energy decreases with $D_{13}$ for $1.6$ Å $< D_{13} < 4.0$ Å and attains a minimum value at $D_{13}=4.0$ Å corresponding to the crystallographic position of Na$_3$. Further increase in $D_{13}$ for $4.1$ Å $< D_{13} < 6.0$ Å results in the increase of the potential energy leading to a maximum at $D_{13}=6.0$ Å. The potential energy decreases with increase in $D_{13}$ beyond $D_{13}=6.0$ Å and attains a minimum value at $D_{13}=8.3$ Å corresponding to the crystallographic position.
Figure 6.17: The interaction energies (potential energy (black), van der Waals (green) and electrostatic (red) energies) of a sodium ion moving along the adiabatic pathway in Model-I (solid lines), and Model-II (symbols): (a) Na-O\textsubscript{PEO} (b) Na-C\textsubscript{PEO} (c) Na-H\textsubscript{PEO} (d) Na-Na (e) Na-I (f) Na-All. All the energy profiles are shifted arbitrarily to set the minimum energy at zero.
of Na$_3$ ion. The Na$_3$-O$_{PEO}$ vdW energy profile exhibits minima at D$_{13}$=3.42 Å and D$_{13}$=7.67 Å with a barrier of 18.86 kcal/mol at D$_{13}$=5.80 Å. The Na$_3$-O$_{PEO}$ electrostatic energy profile consists of a shallow minimum at D$_{13}$=5.20 Å and a deep minimum at D$_{13} > 10$ Å. The interplay of Na-O$_{PEO}$ electrostatic interactions, which favours Na$_3$ to be located at D$_{13}$=5.2 Å, and the vdW interactions, which favours Na$_3$ to be located at D$_{13}$=4.0 Å, results in Na$_3$ to be found at D$_{13}$=4.0 Å.

Let us first examine the total potential energy of the mobile cation (Figure 6.17(f)). In Model-I, the electrostatic energy minimum is observed at D$_{13}$=4 Å and the energy increases steeply on either side of the minimum. A steep rise in the electrostatic potential energy is due to the repulsion with the neighboring Na$^+$ ions. Note that when D$_{13}$=0 Å Na$_3$ overlaps with Na$_1$ giving rise to infinite Na-Na repulsive energy. In Model-II, a minimum is observed at D$_{13}$=4 Å with a finite barrier of 19.01 kcal/mol at D$_{13}$=6.85 Å. The shift of the first minimum to lower D$_{13}$ and of the second minimum to higher D$_{13}$ are due to the creation of excess volume upon formation of ion pair defect. The infinite barrier in Model-I has reduced to a finite value in Model-II due to the formation of ion pair defect in crystalline PEO$_3$:NaI. The vdW energy minimum is observed at D$_{13}$=4 Å in all systems. The vdW barrier at D$_{13}$=6.3 Å is 42.5 kcal/mol in Model-I while significant reduction in vdW barrier is observed in Model-II. The vdW energy steeply increases at D$_{13}$=7.6 Å in Model-I due to atomic overlap whereas minimum energy is observed at this distance in Model-II. The smaller electrostatic and vdW barriers in Model-II allow the cations to readily diffuse to the vacancy during the course of MD simulation. The Na-Na electrostatic repulsion together with the vdW repulsion due to atomic overlap results in a harmonic potential energy well with a minimum located at D$_{13}$=4 Å in Model-I (Figure 6.17(d)). The formation of cation defects in Model-II results in an electrostatic minimum in the barrier region (5 Å < D$_{12}$ < 7.2 Å) thus Na-O$_{PEO}$ and Na-I electrostatic interactions play a catalytic role in reducing the energy barrier for ion transport in Model-II. The vdW energy profiles for the defected crystal overlap with Model-I data for D$_{13}$ < 5.4 Å. The Na-O$_{PEO}$ and Na-I vdW interactions mainly contribute to the overall vdW barrier for ion transport in PEO$_3$:NaI. Since the Na-Na vdW energy is almost zero for D$_{13}$ < 6.5 Å, the removal of a sodium ion did not change the vdW barrier in the defected crystal.
Na-C\textit{PEO} and Na-H\textit{PEO} vdW energies do not contribute much to the energetics of ion transport in SPEs but their electrostatic interactions contribute minimally to the overall energetics of cation transport. The electrostatic contributions of Na-C\textit{PEO} and Na-H\textit{PEO} interactions to the barrier are an order of magnitude less than those from Na-O\textit{PEO} and Na-I electrostatic interactions. The Na-C\textit{PEO} energy profile shows minima at $D_{13}=3.20 \text{ Å}$ and $D_{13}=7.5 \text{ Å}$ with a barrier of 1.85 kcal/mol at $D_{13}=5.20 \text{ Å}$. Similarly, the Na-H\textit{PEO} adiabatic energy profile shows minima at $D_{13}=3.53 \text{ Å}$ and $D_{13}=7.80 \text{ Å}$. These observations indicate that Na-C\textit{PEO} and Na-H\textit{PEO} electrostatic interactions contribute to the stability of cations in their crystallographic positions. The Na-I vdW profile shows two barriers at $D_{13}=2.40 \text{ Å}$ and $D_{13}=6.65 \text{ Å}$ with a minimum at $D_{13}=4.5 \text{ Å}$ and a flat region for $D_{13} > 8.2 \text{ Å}$. The electrostatic profile shows a minimum at $D_{13}=6.60 \text{ Å}$ and barriers at $D_{13}=4.6 \text{ Å}$ and $D_{13}=9.0 \text{ Å}$. The Na-I electrostatic interactions decrease the net barrier to 14 kcal/mol. The high vdW barrier in Na-I profile is due to the large size of the I$^-$ ions. The Na-Na interaction profile shows a steep harmonic well with a minimum at $D_{13}=4.25 \text{ Å}$ in Model-I indicating that the Na-Na repulsion is minimum at $D_{13}=4.25 \text{ Å}$. The steep rise in potential energy is due to the strong electrostatic repulsion between Na$_3$ (sodium ion moving along the adiabatic pathway) and Na$_2$ (sodium ion at its original crystallographic position) ions and the steepness or the curvature of this harmonic well quantifies the degree of retraining (or confining) effect of Na-Na repulsion on the mobile cation. The Na-Na vdW energy is almost zero for $D_{13} < 6.8 \text{ Å}$ but raises steeply beyond $D_{13}=6.8 \text{ Å}$ to infinity at $D_{13} \sim 8.41 \text{ Å}$ (due to atomic overlap of ions) and begins to decrease from thereof. This harmonic well becomes shallow and its minimum is shifted to $D_{13}=6.32 \text{ Å}$ in Model-II whereas the vdW surface has become flat in Model-II.

In summary, the Na-Na electrostatic repulsion and Na-O\textit{PEO} and Na-I vdW interactions provide confining potential energy surface for the cations to remain in their crystallographic positions while Na-O\textit{PEO} and Na-I electrostatic interactions play a catalytic role in reducing the activation barrier by exhibiting energy minimum in the barrier regions. The Na-O\textit{PEO} and Na-I vdW interactions contribute significantly to the barriers (20-40 kcal/mol) in PEO$_3$:NaI due to the proximity of NN O\textit{PEO} atoms and I$^-$ ions to the mobile cation. The differences between Na-O and Na-I vdW profiles can be attributed to the differences in the coordination
number, proximity, and size of NN O_{PEO} atoms and I\textsuperscript{−} ions. The cation defects decrease the activation barrier and shift the minima thus facilitating the displacement of cations toward the void.

6.3.8 Conformational response of polymer to ion transport

Since the conformational flexibility of the polymer is likely to play an important role in the conduction of ions in SPEs,\textsuperscript{223–225} it is desirable to characterize the defect- and hopping-induced changes in polymer conformation in the vicinity of the vacancy site. For this purpose, the variations in the helical pitch (P\textsubscript{h}), radius of gyration (R\textsubscript{g}), and backbone dihedral angle distributions, P(\phi), of PEO\textsubscript{D} in Model-II were examined. In the perfect crystal, P\textsubscript{h} and R\textsubscript{g} fluctuate around their mean values of 7.85±0.3Å and 11.03±0.08Å, respectively (Figure 6.8), which are in good agreement with the corresponding experimental values of 7.98Å and 11.72Å, respectively.\textsuperscript{109} In Model-II, like D\textsubscript{13} and D\textsubscript{24}, P\textsubscript{h} fluctuates (Figure 6.9(d)) around three different values (7.78±0.30Å, 7.65±0.33Å, and 7.17±0.51Å corresponding to the O-, D-, and I-states, respectively) and exhibits abrupt changes between these values at the same time at which ion hopping was observed. Similarly, R\textsubscript{g} also fluctuates (Figure 6.9(h)) around three values (10.93±0.08Å, 10.81±0.08Å, and 10.65±0.09Å corresponding to the O-, D-, and I-states, respectively) and undergoes abrupt transitions coinciding with the ion hopping.

The synchrony between the transitions observed in P\textsubscript{h} and R\textsubscript{g} and ion hopping indicates a strong correlation between polymer dynamics and ion transport in the crystalline PEO\textsubscript{3}:NaI. The mean values of P\textsubscript{h} and R\textsubscript{g} are the lowest and the highest in the I-state and O-state, respectively, indicating that the polymer is compressed along the chain axis in the I-state and it is stretched in the O-state. This observation implies that when the system evolves from the D-state to the O-state via the I-state, P\textsubscript{h} and R\textsubscript{g} decrease during the D→I transition and increase during the I→O transition giving rise to a breathing-like polymer dynamics involving the compression and expansion of PEO along the chain axis. This breathing-like polymer dynamics is likely to play an important role in facilitating ion transport in crystalline PEO\textsubscript{3}:NaI.\textsuperscript{73}

To probe the conformational response of PEO\textsubscript{D} to defect-induced ion hopping in Model-
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Figure 6.18: (A) (a-d) Time evolution and (e-h) the distributions (Model-I (black) and Model-II (red)) of C-O/O-C dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO\(_D\) that are sensitive to defect formation and ion hopping.

II, the time evolution and the distributions of backbone dihedral angles of PEO\(_D\) were examined. Figure 6.18 (e-h) compares the distribution of the C-O/O-C dihedral angle (\(\phi\)) for a few defect-sensitive C-O/O-C dihedrals near the void while the time evolution of these dihedrals are shown in Figure 6.18 (a-d)). In Model-I, \(P(\phi)\) of all C-O/O-C dihedrals are centered at around \(\phi=180^\circ\) suggesting that the O-C/C-O dihedrals of PEO exist in the *trans* conformational state. In Model-II, however, \(P(\phi)\) for a few specific dihedrals (color-coded in Figure 6.18(B)) are shifted with respect to the corresponding \(P(\phi)\) in Model-I while \(P(\phi)\) for all other dihedrals are unperturbed upon defect formation. The defect-induced conformational changes observed for a few void-proximal C-O/O-C dihedrals of PEO\(_D\) suggest that such conformational responses of PEO may be necessary for ion hopping in Model-II. Although the degree of defect-induced conformational shift is different for different C-O/O-C dihedrals, large-scale *trans*=*gauche* conformational transitions in C-O/O-C dihedrals of PEO\(_D\) were not observed during the course of MD simulation. The occurrence of ion hopping in the absence of *trans*=*gauche* conformational transitions suggests that small-amplitude confor-
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Figure 6.19: (A) The distributions (Model-I (black) and Model-II (red)) of C-C dihedral angles for a few backbone dihedrals (color coded in (B)) in PEO_D proximal to the void.

Conformational shifts exhibited by a few defect-proximal C-O/O-C dihedrals are sufficient for the onset of ion hopping in crystalline PEO_3:NaI. The amplitude and frequency of ion hopping is likely to increase in the presence of large-amplitude \textit{trans$\leftrightarrow$gauche} conformational transitions. The observation of small-amplitude C-O/O-C dihedral shifts in PEO facilitating ion transport in crystalline PEO_3:NaI adds to the common notion that large-scale conformational transitions (or segmental motion) are necessary for cation transport in SPEs.\textsuperscript{56,57,69}

We now examine the distributions (Figure 6.19) and the time evolution (not shown) of C-C dihedral angles of PEO_D. Most C-C dihedrals in PEO_D fluctuate around the g state ($\phi=300^\circ$) while some populate the g\textsuperscript{−} state ($\phi=60^\circ$) and \textit{trans$\leftrightarrow$gauche} transitions were absent during the course of MD simulation. $P(\phi)$ for individual C-C dihedrals in Model-II were almost identical to the corresponding distributions in Model-I indicating that the C-C dihedrals are insensitive to defect formation and their role in facilitating ion transport is likely to be relatively less compared to the C-O/O-C dihedrals in crystalline SPEs. Since the C-C conformational barrier
6.4. Conclusions

In summary, the comparison of the computed lattice parameters, radial distribution functions (RDFs), and the polymer dihedral distributions against the corresponding experimental data suggest that the force field parameters used in the present study realistically stabilize the expected PEO$_3$:NaI crystalline state. The MD-derived diffusion paths of the ions reveal that anions follow a helical pathway mirroring the helical symmetry of the polymer. The anion helical path and the PEO helix are intertwined to form a double helical-like column facilitating the cation transport within it which gives a unique conduction mechanism in crystalline PEO$_3$:NaI. The electrostatic imbalance near the vacancy is the molecular basis for the chain length independent helical transport of ions. The free energy profiles and activation energies for the cation and anion transport along the polymer tunnel, and crucial factors determining the free energy barriers are characterized using the ABF method. The defect-induced structural variations and changes in the conformational flexibility of PEO are also investigated.

Figure 6.20: Dihedral energy U(\phi) profiles for the C-C and C-O torsions in PEO$_3$:NaI.

is relatively higher than the C-O/O-C barriers in PEO (Figure 6.20)$^{123,124}$ the C-C dihedrals essentially provide the conformational stability to PEO while the conformational flexibility of C-O/O-C dihedrals is leveraged for facilitating ion transport in crystalline SPEs.

6.4 Conclusions
The direct observation of defect-induced changes in polymer conformation and migration of ions in crystalline PEO$_3$:NaI has unfolded interesting clues about the coupling between polymer dynamics and ion hopping in SPEs. In light of recent advances in new experimental techniques including the aberration-corrected transmission electron microscopy, radioactive tracer experiments and 4D-electron microscopy to image atomic diffusion and polymer conformations in solids, the timely study carried out here provides energy landscape-based insight into polymer-coupled ion transport in SPEs. We anticipate that the microscopic observations made in this work can be helpful in technological exploitation of these materials.