Order-Disorder Transitions and Melting in a Helical Polymer Crystal: Molecular Dynamics Calculations of Poly(Ethylene Oxide)

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Abstract

Structural transitions and the melting behavior of crystalline poly(ethylene oxide), \((\text{CH}_2\text{-CH}_2\text{-O})_n\), (PEO) has been investigated using fully atomistic, constant pressure-constant temperature (NPT) molecular dynamics (MD) simulations. Melting of PEO proceeds in two stages; Order parameters reveal the loss of interchain orientational correlations and of chain helicity in the first and second stages of melting respectively. Sliding diffusion and anisotropic reorientational dynamics of the polymer backbone are observed in the solid state, in agreement with \(^1\text{H}\) NMR experiments.

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Relaxation processes in helical solid polymers such as poly(tetrafluoroethylene) (PTFE), poly(ethylene oxide) (PEO), and polypropylene, have been studied extensively over several decades [1, 2]. Conformational transitions in crystals of such polymers and of long chain molecules can lead to molecular mobility in the solid state [3]. The coupling between intramolecular order and intermolecular interactions in such systems can induce structural transitions within the solid state, leading to a rich phase diagram [4, 5]. For instance, in PTFE, x-ray diffraction and calorimetry have shown the existence of three solid phases at atmospheric pressure [6]. Recent atomistic simulations of PTFE have been able to reproduce the existence of these phases, and have provided microscopic structural data that differentiates them [7].

The chains in PEO, unlike those in PTFE, have a distorted helical conformation in the crystalline phase. The melting point of PEO is around 340K, with a dependence on the molecular weight and on the morphology of the crystal [8]. The calorimetric trace of low molecular weight PEO containing extended chains, exhibits a hump or a long tail at temperatures below the melting transition [9], which suggests that melting could involve stages of microscopic events.

Early studies on $^1$H NMR line widths of PEO had shown a sudden decrease at 270K, much below its melting point [10]. Calorimetric [9, 11], diffraction [12], and spectroscopic [13] measurements as well have shown signatures of premelting transitions, that lead to molecular mobility in the solid state. Our aim here is to provide complementary, microscopic data to identify such a transition in the crystalline phase of PEO. In an effort to understand the structural changes accompanying this transition, we have performed atomistic molecular dynamics simulations of PEO as a function of temperature [14]. Two transitions are observed – one associated with interchain ordering, and the other with intrachain ordering. The intermediate phase, although crystalline, exhibits interesting translational and rotational dynamics.

Figure 1 presents the internal energy of the system, divided into intermolecular and bonded intramolecular contributions as a function of temperature. The latter is a sum of contributions from stretch, bend, and torsional interactions. Its dependence on temperature is monotonic, indicating the gradual population of defect states, while two clear discontinuities can be seen in the behavior of intermolecular energy. This shows that the simulated PEO melts in two stages. This is also evident from the evolution of the lattice parameters as a function of temperature shown in Figure 1. The $c$ parameter, along which the polymer chains are aligned, shows a large decrease only at around 470K, i.e., during the second stage of melting. However, the $a$ and $b$ parameters exhibit a behavior similar to the intermolecular energy, with two discontinuities, one at 390K, and another at 480K, indicating again, the relationship between intermolecular order and the transition at 390K. These two stages of melting are also seen in the variation of the volume of the system. Based on the changes in both the internal energy and in the volume of the system, we estimate the enthalpy change to be 3.0 kJ/mol of monomer for the transition at 390K, and 6.2 kJ/mol of monomer for the second stage of melting at 480K. The sum of these values are in reasonable agreement with the experimental value of 8.7 kJ/mol of monomer[15]. We have characterized the nature of these transitions

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using order parameters (Figure 1f) that describe intermolecular orientations, as well as an intramolecular characteristic, viz., the helicity of the chains, both of which have been introduced by Sprik et al earlier [7]. The interchain order parameter is obtained by studying the ordering in the orientation of the bisector of methylene groups that belong to chains separated by distances of the order of 10Å. The helical order parameter studies the angle between vectors that bisect successive triplets of atoms in a polymer backbone. Consistent with our observations earlier, we find that the interchain orientational order collapses at the premelting transition, while the helical or intramolecular ordering vanishes at the melting transition. Thus, it appears that although the interchain CH₂ orientational ordering is lost at around 390K, the chains retain their helicity and their orientation along the c-axis through this premelting, solid-solid transition [11].

The loss of interchain ordering, seemingly innocuous, is accompanied by subtle conformational transitions in the polymer chains. At room temperature, the torsions around the C-C and the C-O bonds are in gauche (g) and trans (t) states respectively, with the sequence, ttg for successive bonds in the chain producing the basic helical conformation. In the crystal, the C-O torsional angle is found to have a value of $186.6^\circ \pm 7.8^\circ$ [17]. This width in the torsional distribution manifests as a distortion in the helical conformation and is attributed to the flexibility of the PEO chains and to strong intermolecular interactions [17]. It is thus natural to ask if the observed loss of ordering in interchain CH₂ orientations results in the reduction of this distortion. The distributions of C-O torsional angles obtained from our simulations at different temperatures, are displayed in Figure 2a [16]. We observe that torsional sub-states present near angles of $150^\circ$ and $210^\circ$ that were presumably frozen by strong intermolecular interactions, are populated at 310K and 380K, but become less likely at 390K and at 410K. This implies that the polymer chains are less distorted with increasing temperature within a narrow window of 20K around 400K. Cross sectional views of the crystal in the ab plane shown in Figure 2b shows the distortion in the molecular conformation at 380K, while at 410K, a good fraction of the molecules exhibit a smoother, nearly circular pattern. This change can be attributed, among other possibilities, to a reduction in the distortion in the helix, consistent with the results on C-O torsional distributions observed in Figure 2a. The simultaneous emergence of this intramolecular, “nearly ordering” transition and the loss of orientational order between chains, further validates the original observations of Takahashi and Tadokoro [17] that the conformational distortion is brought about by interchain forces. At temperatures higher than 410K, the number of C-O torsions in the gauche state increases gradually, thus decreasing the helicity of polymer chains. The chains approach a random coil configuration (not shown), causing the c-parameter of the crystal unit cell to decrease. The helical order parameter vanishes at around 480K, signifying the completion of the melting process.

The structural changes through the two stages of melting bring forth interesting behavior in the dynamics of the polymer chains. Specifically, the loss of orientational ordering between chains at 390K and their adoption of smoother contours allows them to slide past each other along the direction of the c-axis in the crystal.
Figure 3, we show the displacements of the centers of mass of the polymer chains along the c-axis, and in the ab plane at a few selected temperatures, across the two transitions. We find that the displacement curve for motion along the c-axis exhibits a positive slope at 390K, which is absent at 380K. This shows that the premelting transition is reasonably sharp. As expected, the molecular displacements in the ab plane is minimal up to even 410K. The lateral motion increases in magnitude only much after the premelting transition. Our data on the sliding diffusion of chains is in good agreement with numerous experimental observations [18, 19]. The anisotropy in molecular displacements that sets in at 390K and its continuance up to the melting transition at 480K is evident and explains the NMR and calorimetric observations [10, 11].

We further probe the dynamics of the system through time correlation functions (TCF) of the bisector (\(\vec{R}\)) of triplets of consecutive atoms along the polymer backbone. In Figure 4, we display the normalized time correlation functions of the projection of \(\vec{R}\), on to the c-axis, and its residual in the ab plane. We denote these as \(C_c(t) = \langle R_c(0)R_c(t) \rangle\) and \(C_{ab}(t) = \langle \vec{R}_{ab}(0)\vec{R}_{ab}(t) \rangle\) respectively. At 310K and 380K, the function in the ab plane does not relax for over hundreds of picoseconds, as expected for a rigid solid. The \(C_c(t)\) function, on the other hand, relaxes to a constant, non-zero value after about 1 ps at these temperatures. Its value at long times is considerably smaller than that for the \(C_{ab}(t)\) function, indicating the greater spread of angles that the bisector can probe along the c-axis. This enhanced angular freedom along the c-axis is presumably due to the relative ease of the atoms of the chains to buckle back and forth, rather than to make long amplitude vibrations along the c-axis. This observation is in good agreement with rms amplitudes of vibrations obtained from x-ray diffraction studies in the isostructural polyoxymethylene crystal [20], and from the splittings of the perpendicular bands observed in the infrared spectra of PEO at low temperatures [13]. At 390K, the \(C_{ab}(t)\) function relaxes slowly to a non-zero value, implying that the projection of the bisector vector in the ab-plane is able to probe only a large portion of a circle in the plane, and not the entire range of 360°. At 410K and above, the function decays to zero, a consequence of the rotation of the polymer chains about their long axis. This rotation is facilitated by the formation of the cylindrical contour of the chains, as discussed in Figure 2. A surprising observation is that the \(C_c(t)\) function exhibits a slower decay with increase in temperature between 410K and 480K. This apparently anomalous observation can be rationalized if one considers that the formation of gauche defects along the chain decreases the c lattice parameter, and increases the density of the system along this direction, thus slowing the relaxation of the \(C_c(t)\) function. At 480K, the dynamics along the c-axis and that in the ab plane, are nearly identical, indicating the attainment of isotropy in the system.

To summarize, large scale, atomistic MD simulations of PEO crystal at more than 30 temperatures, have revealed interesting conformational, and intermolecular transitions that profoundly influence the dynamics of the polymer chains. Melting of the crystal takes place in two stages [21]. In the first stage, at 390K, we observe a discontinuous, solid-solid transition, much like first order, with signatures
in thermodynamical and structural quantities. Unlike Sprik et al [7], we observe a clear discontinuity in this first stage of the transition, probably due to the finer temperature resolution that we were able to employ. This premelting transition is associated with the loss of interchain orientational ordering, and is accompanied by an interesting change in the conformation of the chains – over a narrow temperature range around 400K, there is a small reduction in the helical distortion. This transformation aids the translational diffusion of chains along their long axes. The second stage of melting is completed at 480K, where the helicity of the chains is entirely lost, resulting in randomly oriented chains. Consequently, the $c$ lattice parameter decreases monotonically during this stage between 400K and 480K. The ability of the chains to rotate about and diffuse along their long axes is established at 390K. The TCF of the backbone vector along the long axis of the chains exhibits a seemingly anomalous temperature dependence during the second stage of melting, i.e., with increasing temperature, it relaxes slower. However, this can be rationalized in view of the increase in density along the $c$-axis during this phase. The results reported here are comparable to experimental data on single crystals of extended chain PEO. Calorimetric traces of such low molecular weight PEO have exhibited a hump or a long tail at temperatures below the melting transition [9].

Despite differences in the crystal structures and in the conformations of chains, the structural phase transitions observed for PEO here bears some similarities to those seen in PTFE by Sprik and coworkers [7]. It is to be noted however, that the high temperature phase of PTFE is columnar with hexagonal symmetry [22], while that in PEO continues to be a three dimensional crystal. The similarity of these phase transformations suggest that the phenomena observed might be universal and could be applicable to crystals of biologically relevant, small organic molecules possessing helical conformations. The sliding diffusion [18, 19] of polymer chains in the orientationally disordered solid phase adds support to the mechanisms of folding transitions observed in metastable forms of PEO [8, 23] and of crystallization kinetics in polymers [24].

We thank Professor Biman Bagchi for helpful comments on an earlier version of this manuscript, and the CSIR, India for partial financial support.
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[14] MD simulations, using the PINY_MD code [25] were performed under NPT conditions in a fully flexible cell using the Parrinello-Rahman method, at temperatures ranging from 300K, starting from the crystal structure [17], and heated up to 490K in steps of 5K for a system containing 4 unit cells along a, and 2 unit cells each along b and c axes. The total number of atoms was 3136, which included hydrogen atoms explicitly. The ends of each polymer chain were bonded to each other, across the boundary to remove end effects [26]. Long range interactions were treated using the Ewald method with an α of 0.3 Å⁻¹, and 2399 reciprocal space points were included in the Ewald sum. The potentials of interaction are the same as used in Ref. [27] with torsional parameters from the CHARMM data set [28]. The equations of motion were integrated with a multiple time step scheme, employing an outer time step of 3 fs. At each temperature, the system was equilibrated for 100 ps. Analyses runs of length 30 ps were performed after equilibration at temperature intervals of 10K, and
configurations were stored every 300 fs from which energies and structural quantities were calculated. Dynamical quantities were calculated for temperatures reported in Figures 3 and 4, from a trajectory of length 300 ps with an interval of 1.5 ps. Other details of the simulations can be found in M. Krishnan, and S. Balasubramanian Phys. Rev. B 68, 064304 (2003).

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Figure 1: Lattice parameters of unit cell (a) $a$ (b) $b$ (filled circles) and $c$ (open circles), and (c) Volume of the simulation cell (d) Intermolecular energy (e) Bonded intramolecular energy, (f) Interchain orientational order parameter (open circles) and helical order parameter (filled circles) against temperature. The order parameters are normalized with respect to their values at 310K.
Figure 2: (a) Distribution of C-O torsional angles, obtained from time averaged configurations [16] for temperatures indicated. (b) View through c-axis of time averaged configurations at two temperatures.
Figure 3: Mean square displacement of centers of mass of PEO chains along the c axis (solid lines) and in the ab-plane (dashed lines) for temperatures indicated.
Figure 4: Normalized rotational time correlation functions, $C_c(t)$ (solid lines) and $C_{ab}(t)$ (dashed lines) at different temperatures.