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Molecular simulation studies of glassy

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Critical Review of the paper:

The article "**Detailed Atomistic Simulation of the Segmental Dynamics and Barrier Properties of Amorphous Poly(ethylene terephthalate) and Poly(ethylene isophthalate)**" seeks to address "t*he structural, conformational, dynamic, and barrier properties of the amorphous (glassy and melt) phases of two polyisomers, PET [poly(ethylene terephthalate)] and PEI [poly(ethylene isophthalate)]*", as mentioned in its abstract (p.2978). In the introduction section, article clearly explains the importance of this study by giving a wide variety of applications of Poly(ethylene terephthalate) (PET) is used in the assembling and bundling enterprises because of its unrivaled obstruction properties in examination with other polymers, but losing its competitive edge in the market to a structurally similar polymer Poly(ethylene-2,6-naphthalene) (PEN) due to its improved quality, warm dependability, and hindrance properties, all at the expense of the higher expense related with the generation and utilization of PEN. In-order to overcome this disadvantage associated with PEN, industries started favoring copolymers or blends based on PET especially PETI (a copolymer based on the blends of PET and PEI). The primary reason for favoring this copolymer is the improved barrier properties. Schematic representation of the PET and PEI repeat units is shown in Figure 1. The present article elucidates the molecular level mechanism responsible for the improved barrier properties of Poly(ethylene isophthalate), PEI, as compared to PET which also answer the question why PET-PEI copolymers shows enhanced barrier properties in comparison with pure PET. The authors have used a fairly improved methodology to carry out this work which includes the utilization of a point by point constrain field, age of sensible atomistic designs and the detailed analysis of the static (density, conformational properties, structural properties), dynamics (phenyl ring motions) and barrier properties (oxygen diffusivity) of the two polyesters by performing appropriate statistical averaging over several uncorrelated configuration.
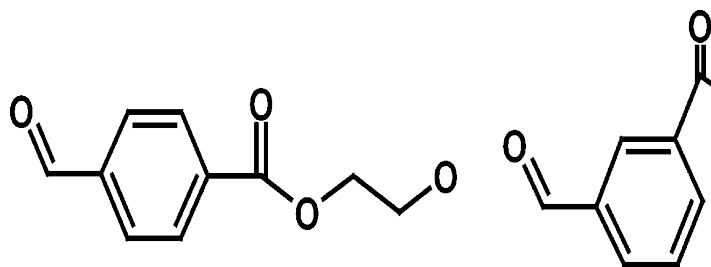
Figure 1. Schematic of the PET (left) and PEI (right) repeat unit

In the second section of the article authors gives a detailed mechanism of how diffusivity studies are carried out using Molecular dynamics (MD) simulations and transition state theory (TST). Diffusion is a phenomena that encompasses a wide range of time and length scales which exceeds by numerous requests of extent the scales that can be followed by atomic elements. Diffusivity of a penetrant molecule through a polymer matrix is governed by the size of the penetrant molecule, interactions with the polymer matrix, shape, size, connectivity and the time scales of thermal rearrangement of accessible volumes in the polymer matrix. The accessible volume in the polymer matrix can be divided into static volume and the dynamic volume. Static volumes are the volumes that are permanently available in the polymer matrix while the dynamic volumes are the volumes that gets available in the polymer matrix because of the conformational changes as well as because of the segmental mobility in the polymer matrix. If the temperature is high enough (well above the T_g) causing rapid local thermal motion in the polymer matrix then the static volume in the polymer matrix gets connected to the other static volumes by a channel formed between them as a result of the dynamic volume created, because of the conformational changes and the segmental mobility. It is easier to perform diffusional studies on high temperature melt rather than the glassy polymer because the glassy polymers are much less mobile than the high temperature melt as in the case of glassy polymers in which their configurations are trapped in regions of local potential energy with transition from one minima to another restricted by the high energy barriers. Therefore, the distributions of the accessible volumes remain largely unaltered and the formation of channels between these volumes occurs very infrequently in the glassy phase. The regions of accessible volumes in the polymer matrix is evaluated by using the TST method in which a 3-D grid of high resolution is laid on the polymer matrix covering the whole volume of the simulation cell. Next a test particle resembling the

penetrant is inserted at each point on the framework and the subsequent nonbonded associations with all the polymer iotas is computed which results in the formation of the potential energy surface. The regions of minimum energy on this potential energy surface are the accessible volume regions for the penetrant and the excluded volume regions are the high interaction energy regions which should be avoided by the penetrants. Along with the thermal motions of the atoms of the polymer chains the small penetrant molecules are also carried along by jumping from one cavity to another as a result of the thickness vacillations on the length size of the penetrant estimate. For calculating the diffusivity, the smearing factor was calculated by utilizing the information about the mean square displacements of the polymer atoms from their equilibrium positions. Using the smearing factor all possible sorption sites in PET and PEI were identified and diffusivity was anticipated by running motor Monte Carlo reproductions along with the evaluation of the mean square displacement of about 2000 penetrant molecules on the network of microstates.

In the next section the authors talks about the methods to generate the well equilibrated glassy and melt samples of PEI and PET. Initially a parent chain consisting of 80 repeating units is prepared in the amorphous builder module of Cerius 2 with sufficiently low density to avoid unrealistic packing of atoms along the chain. The structure is then energy minimized and followed by the alternate NVT and NPT run until the samples reaches their corresponding experimental density. At first the twelve-step Hofmann equilibration cycle is applied to the samples followed by an extended equilibration cycle to get the fully relaxed sample equilibrated at all length scales. Steps involved in the Hofmann equilibration cycle is shown in Table 1. The extended equilibration cycle consisted of increasing the box volume followed by the energy minimization step. The energy minimization step is followed by high temperature NVT run from which four uncorrelated configurations are extracted which are further subjected to NPT run to get the desired experimental density followed by energy minimization and NVT MD simulation run. Finally a long production run of 3 ns is simulated to get the properties of interest at the desired temperature and pressure. The results are averaged over all the uncorrelated configurations to get the better statistical averaging. Entire simulation steps are performed using PCFF forcefield.

Table 1: Hoffman Equilibrium Cycle

equilibratio s	simulatio condition	durati (
1	NVT 600	5
2	NVT 300	5
3	NPT 1000 bar 300 K	5
4	NVT 600	5
5	NVT 300	1
6	NPT 30000 bar 300 K	5
7	NVT 600	5
8	NVT 300	1
9	NPT 5000 bar 300 K	5
1	NVT 600	5
1	NVT 300	1
1	NPT 1 bar 300 K	10

The results and discussion section starts with a discussion on the various static properties of the polymers such as density, conformational properties and the structural properties. The density of the samples obtained after Hoffman equilibration cycle is found to be in good agreement with the experimental density of both the polyesters. In the conformational property part the mean square end-to-end distance, characteristic ratio and various torsion angles were evaluated. Mean square end-to-end distance did not show much variation at the time scales of the production run indicating the inability of the MD to equilibrate the samples at all length scales within a production run time of 3 ns. After averaging the mean square end-to-end distance over all the independent configuration, the characteristic ratio was calculated which is found to be in good agreement with the experimental values. Different torsion angles evaluated for both the polyesters were found to be similar. Structural properties of the two polyesters was studied using total radial distribution function (RDF). The total RDF is found to be similar for the two

polymers at all distances except in the range of 5-6Å which may be caused because of the different attachment of the ester group to the phenyl ring in the two polymers. From the static properties it can be seen that the static structure of the two polymers are almost identical and therefore the distribution of the static volumes in the two polyesters should not be expected to be widely different,which cannot explain the difference in barrier properties of the two polymers. In-order to further explore the reason behind the different barrier properties of the two polyesters local segmental dynamics in PET and PEI melts (at 450K and 600K) is observed by using the time autocorrelation functions for different torsion angles, the unit normal vector to the phenyl ring and the ester group. It was observed that at 600K the PET melt showed higher local segmental mobility both in terms of the ring flips and the higher amplitude of the torsional librations when compared to PEI. While at 450K although the ring flips were not observed in the PEI and PET melts, the torsional librations in PET melt was found to be higher than the PEI melt. This explains clearly the enhanced barrier property of PET when compared to PEI.

In the last section of the result diffusivity value has been calculated for oxygen diffusion through the polymer matrix by using the TST approach. In this method the thermal fluctuation of the atoms in the polymer matrix about their equilibrium position was calculated by the use of the single parameter namely smearing factor, which was calculated by running short MD runs for the time equal to the most probable residence time of the penetrant in the sorption sites. The smearing factor obtained gives an indication of the portability of the polymer grid i.e., on the plentifulness of vibrations, torsional librations and on the recurrence of advances between various conformational states, which subsequently is responsible for the channel formation between the microstates. Oxygen diffusivity is evaluated by using the mean square displacement of about 2000 penetrant molecules on the network of microstates. The diffusivity value obtained from the simulations is found to be in good agreement with the experimental results for the samples obtained with the extended equilibration cycle. While the diffusivity values obtained for the samples prepared without the extended equilibration cycle, were not found to be in agreement with the experimental values, although the density for these samples were found to be in good agreement with the experimental values, with error being less than 2%. This explains the importance of the proper equilibration of the samples at the accurate density (which matches with the experimental values).

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