Molecular Dynamics Simulations for Glass Transition Temperature Predictions of Polyhydroxyalkanoate Biopolymers

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S1 Chemical Structures of PHAs



Figure S1: Two-dimensional chemical structures of building blocks that form PHAs which have been considered in this study.

S2 Methods and Model Details

S2.1 Additional Computational Details

The force field (FF) parameters of CHARMM General Force Field (CGenFF) were obtained by uploading the coordinates on "https://cgenff.umaryland.edu/".^{1,2} GAFF parameters were generated using AmberTools^{3,4} while the partial charges on the atoms were derived using R.E.D. Server Development 2.0.^{5,6} On the other hand, PCFF parameters were obtained using Enhanced Monte Carlo (EMC) code while generating the initial configurations of amorphous polymer box.^{7,8} Trimer model illustrating the capping of polymer chains with hydrogen and methoxy (-OCH₃) groups on either side is shown in **Figure** S4. The real space cutoff for non-bonded interactions was 12 Å for CGenFF and GAFF, while it was 9.5 Å for PCFF.



Figure S2: Potential energy of amorphous box consisting of 20 P4HB chains. Each chain is made of 100 monomer units (100-mer). Simulations were performed at 700 K using mPCFF parameters.



Figure S3: Prediction of T_g values for five different initial configurations. Simulated system consists of 20 chains (each constructed with 100 monomer units) and thermal quenching rate of 20 K/ns was employed. Amorphous polymer box was made of P4HB polymers modelled using mPCFF parameters.



Figure S4: Trimer model of poly(4-hydroxybutyrate) (P4HB) capped with hydrogen and methoxy (-OCH₃) end groups.

S2.2 Refinement of Torsion Potentials

Qualitative incorrect behavior of PCFF potential energy profiles for dihedrals including the ketone carbon (C=O) were refitted to match with corresponding DFT profiles as described here. E_{DFT} denotes the DFT potential energy profile for a given dihedral. Next, $E_{PCFF}(0)$ refers to the PCFF potential energy profile by removing the contribution from the dihedral of interest. The difference between the above two terms ($E_{DFT} - E_{PCFF}(0)$) represents the new torsion energy profile ($E_{torsion}$) and was fitted using **Equation 1** to obtain the modified torsion parameters. Here, we have refined torsion parameters associated with - CH₂-CH₂-C(=O)-O- and -CH₂-C(=O)-O-CH2- motifs in the backbone chain in a sequential manner. Firstly, the torsion parameters of former have been modified and subsequently, torsion parameters of latter were refitted employing the modified parameters for the former.

TableS1 lists the modified torsion parameters of mPCFF.

$$E_{torsion} = \sum_{n=1}^{3} K_n \left[1 - \cos(n\phi - \phi_n) \right] \tag{1}$$

here n is the multiplicity, K_n and ϕ_n are the force constants and equilibrium dihedral angles.

Table S1: Modified torsion parameters of mPCFF. Force constants are in Kcal/mol and ϕ s are in degrees.

Dihedral type	K_1	ϕ_1	K_2	ϕ_2	K_3	ϕ_3
$-\mathrm{CH}_2\text{-}\mathrm{CH}_2\text{-}\mathrm{C}(=\mathrm{O})\text{-}\mathrm{O}\text{-}$	-0.469	0.00	1.96847	0.00	0.22716	0.00
-CH ₂ -C(=O)-O-CH2-	-5.05826	0.00	3.40145	0.00	-0.24052	0.00

S3 Dependence of T_g Predictions on Various Simulation

Parameters



Figure S5: Prediction of T_g values by changing the number of polymer chains in the system. Each chain consists of 100 monomer units (100-mer) and thermal quenching rate of 20 K/ns was employed. Amorphous polymer box was made of P4HB polymers modelled using mPCFF parameters.



Figure S6: Prediction of T_g values by varying the polymer chain-length. Here, thermal quenching rate of 20 K/ns was used. P4HB polymers have been used for this study employing mPCFF parameters.



Figure S7: Dependence of T_g by varying the thermal quenching rate. Simulated system consists of 20 chains (each constructed with 100 monomer units). mPCFF parameters were used to model the P4HB chains.



Figure S8: Comparison of the computed T_g values of PHAs with corresponding experimental ones. Filled and empty symbols correspond to the PHAs with linear side chains and phenyl-capped side chains, respectively.



Figure S9: Number of hydrogen bonds between the carboxyl side chain functional groups in case of P3CoxyP. Donor-acceptor (O-O) distance of 3.5 Å and the angle (O-H...O) greater than 150° were used to determine the presence of hydrogen bonds.^{9,10} Simulations were peformed using mPCFF parameters at (a) 400 K and (b) 700 K.

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