Prediction of Renewable Polymer Properties Using Quantum and Molecular Modeling

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An important trend in the development of new polymeric materials has been a movement toward polymers that are derived from renewable resources. Polylactide (PLA) and a family of polyhydroxyalkanoates (PHAs) have received widespread attention due to their physical properties, ease of synthesis, and formation from low cost agricultural products. Presently, the cost of manufacturing many of these polymers is sufficiently low that their use as commodity polymers is economically viable. Individually many of these polymers are lacking in some physical property, but blends of these materials have been shown to yield the desirable properties. Synthesis and testing of all possible copolymers and polymer blends required for a diverse range of applications would be prohibitively time consuming and expensive. Therefore, a promising alternative is to use molecular modeling to predict the physical and transport properties of these polymer systems.

The Groningen Machine for Chemical Simulations (GROMACS) is a molecular simulation engine designed to take advantage of message-passing, parallel-processing, computer architectures so that large chemical systems can be easily modeled by molecular dynamics (MD) and replica exchange MD techniques. Simulations of polymer properties, including heat capacity, rheological behavior, and small molecule diffusion characteristics, have been conducted using equilibrium and nonequilibrium MD methods. These simulations were conducted using a variant of the OPLS force field, where the force field parameters were optimized specifically for these polymer systems using results from diffraction experiments and extensive density functional theory (DFT) simulations of the respective oligomer systems. Further, the quantum mechanical simulations yielded vital information about the degradation behavior of these polymer systems. The results from all of these simulations provide key insights into structure property relationships for these bioinspired polymer systems.

The goal of the present work is to establish relationships between biopolymer structure and their end properties. As seen in Figure 1, there is considerable freedom in designing PHAs by altering the length of the carbon chain substituents, the stereoconfiguration of its chiral centers, and monomeric sequence within the chain. One property that affects the suitability of PHAs in consumer applications is their susceptibility to molecular degradation. Obviously PHAs are designed to undergo biodegradation when composted, a process which proceeds primarily by a hydrolytic cleavage mechanism. However, they have been known to degrade under normal processing conditions by breaking bonds characteristic of an elimination mechanism[1]. Two possible reaction pathways consistent with this mechanism are shown in Figure 2. Computational analysis at the DFT/B3LYP/6-31G** level is well-suited for exploring this mechanism due to its efficiency and relative accuracy when compared to other methods of similar rigor. A detailed analysis of the reaction path involves mapping out the potential energy surface for the PHA system, determining the appropriate reaction coordinate, and then searching for and identifying the transition state. The DFT-level methods, in conjunction with solvation models and advanced eigenvector-following routines, allow this analysis to be performed on oligomers of modest size in an electronic environment representative of the bulk phase.

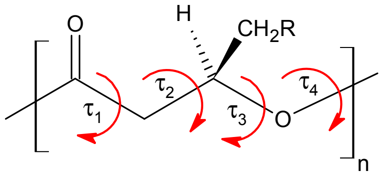

Figure 1. Repeat unit for PHA, where the R group can be hydrogen or a linear alkane with two to fourteen carbons. Also note the chiral center.

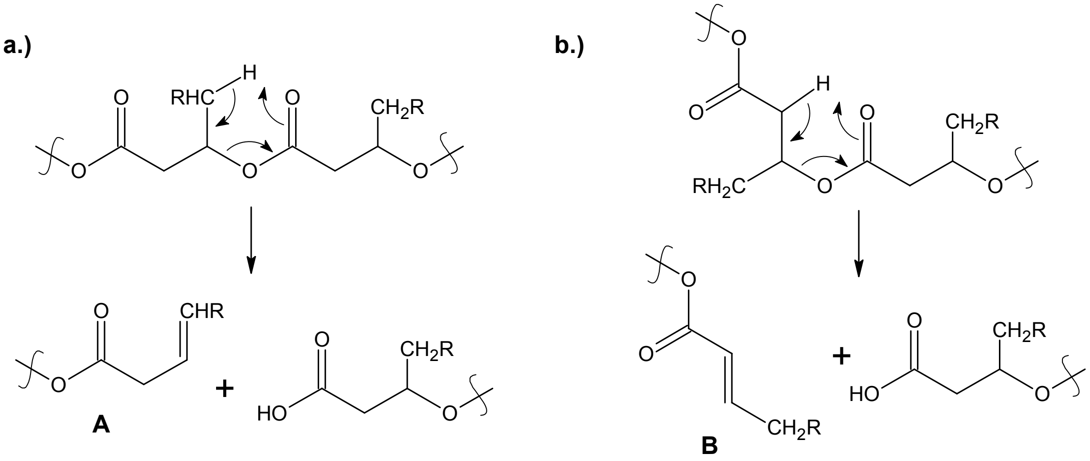

Figure 2. Elimination pathways in PHA

While the above approach can support the elimination mechanism as a viable explanation for in-process degradation of PHAs, a complete energy landscape analysis for all PHAs of interest becomes an inefficient way to approach this sort of problem. Therefore we are inclined to use a more simplistic approach when comparing the degradation kinetics for the large number of polymers that make up this family. For example, the straightforward calculation of bond strengths, rotational barriers, and partial atomic charge distributions can aid in establishing vital relationships between polymer structure and degradation behavior. By analyzing these trends in comparison with experimental degradation rates, it is easy to discern whether the kinetics are governed by the electronic structure as shown in charge distributions, the steric effects evidenced in conformational energy barriers, or both.

The energy profiles for torsional rotation about bond τ_3 are shown in Figure 3 for poly(hydroxybutyrate) (PHB) and poly(hydroxyvalerate) (PHV). Experimentally, it has been observed that PHV degrades faster than PHB during processing. The two major maxima shown on the plots correspond to the dihedral angles found in the elimination-mechanism transition states proposed in Figure 2. Clearly the barrier heights from the native gauche state ($\tau_3 \approx 75^{o}$) to transition state b.) do not show an appreciable difference for PHB and PHV. Though the barrier height to transition state a.) is higher for PHV, this shows that, if anything, steric effects will inhibit degradation of PHV as compared to PHB. Experimentally this is not the case, and thus it seems we must turn to the electronic structure properties of these molecules instead of steric barriers to explain the difference in degradation rates.

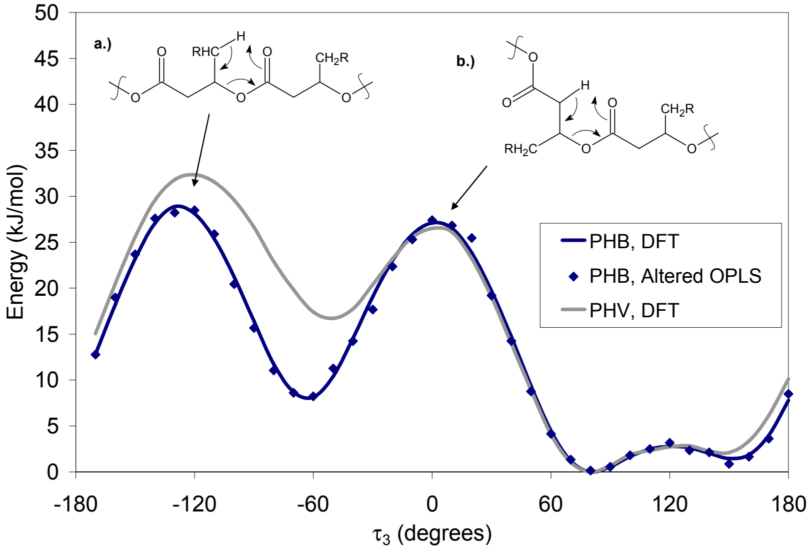

Figure 3. Energy barriers for rotation about bond τ_3. The maxima indicated correspond to the dihedral angles found in the elimination mechanism transition states. The diamonds were computed for PHB using OPLS and the torsional parameters developed in this work.

Bulk properties of PHAs are best modeled with molecular mechanics methods. Given an accurate force-field description exists for the polymer systems, the molecular motions may be calculated using molecular dynamics (MD). Several forcefields exist which are parameterized to reproduce the energetics of a host of organic materials, polymeric or otherwise. Among these, the Optimized Potential for Liquid Systems (OPLS) is a simple point-charge model fit extensively to thermodynamic properties of liquid organics, and the Polymer Consistent Forcefield (PCFF) is an accurate class III potential optimized for synthetic polymers. While both of these perform quite well on a large number of systems, neither has been optimized specifically for the bio-derived polyesters studied in this work. That said, the quality of the nonbonded OPLS parameters reproduce the melt-phase energetics of PHAs quite well, making OPLS suitable for calculation of properties such as miscibilities. However, the stereoregular PHAs have semi-crystalline morphology, and the structural properties of crystalline PHAs are not captured by this forcefield. Simulations initialized with well-established experimental crystal structure coordinates[2] have fallen into disorder within picoseconds. Since conformational properties are strongly dependent on rotational barriers, manipulation of the torsional parameters can improve structural prediction without greatly altering the thermodynamic accuracy of the optimized nonbonded parameters. This method has been successful in simulating thermodynamic and transport properties of PLA, and using our modified parameters the PLA crystal structure is accurately predicted and remains stable during dynamics simulations. Using the same parameters, thermodynamic properties such as heat capacities have retained the accuracy of the of the original OPLS, and the predicted heat capacity for amorphous PLA is 1.77 J/(g K), compared to the value of 1.8 J/(g K) reported in the experimental literature[3].

Currently our focus is on parameterizing a forcefield for PHAs. A comparison of forcefield and quantum-predicted rotational barriers for PHB is included in Figure 3, showing good agreement with the modified OPLS parameters fit in this work. We have also found that the PCFF performs fairly well for solid phase PHAs. Figure 4 shows the crystal structure of PHB as predicted by energy minimization with PCFF, and the backbone dihedral angles are compared to the X-ray diffraction coordinates of Bruckner et. al. in Table I. Though the predicted crystal structure is consistent with the experimentally observed helical repeat cell and P212121 space group symmetry, quantitative agreement with structural parameters show room for improvement. However, the complexity of PCFF due to the presence of cross terms makes parameter refinement difficult, and given the favorable results achieved with PLA we believe that modifying the OPLS dihedral parameters can result in an accurate representation of the material with modest effort. In addition, the OPLS parameters are readily used in the GROMACS simulation software, which will allow us to take advantage of the massive parallel computing architecture available to us.

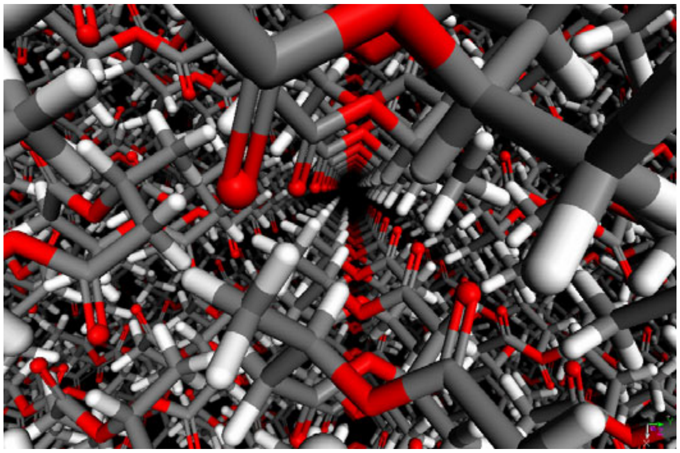

Figure 4. Crystal structure of PHB as optimized by PCFF. This view is in the axial direction of the helical repeat structure.

Table I. Dihedral angles in PCFF-optimized crystal and experimental x-ray structure

Angle	PCFF	Experimental
τ_1	-27°	-35°
τ_2	-60°	-59°
τ_3	157°	149°
τ_4	163°	-173°

In conclusion, our preliminary results show that structure-property relationships for PLA and PHA materials can be determined effectively using available computational tools. We will continue to use these tools to further our understanding of degradation behavior. In addition, the forcefield parameters we have developed for molecular mechanics calculations in GROMACS will allow us to explore a large number of polymer blends and copolymers without the cost of lab measurement

References

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