ADJUSTMENTS TO BOND AND ANGLE PARAMETERS IN PLAFF2 and PLAFF3

This document outlines the adjustments made to the bond and angle parameters in PLAFF2 and PLAFF3, as described in the paper "Development of force field parameters for molecular simulation of polylactide" by J.H. McAliley and D.A. Bruce. The force field parameters for the bonds and angles shown here were adjusted because these bonds and angles deviated from the values in the crystal structure analysis, as well as the equilibrium positions predicted by DFT. The DFT calculations, plotted in the following figures, were carried out at the B3-LYP/6-31G** level using a PLA trimer. Similar to the fitting procedure for the dihedral energy parameters described in the paper, constrained geometry optimizations were used to obtain the DFT energy, and again for the force field energy prior to each force field parameter adjustment.

DFT methods are generally known to give accurate geometries, while they are less accurate at predicting vibrational frequencies. For this reason, each of the following interactions were fit to DFT data by adjusting the geometric parameters (the b_0 parameter for bonds, and the θ_0 parameter for angles) only; the force constants (k_b and k_θ) were unaltered from their original OPLS values. In this way, we deviate as little as possible from the OPLS model. Fitting each bond or angle interaction requires the use of a self-consistent iterative scheme, much like that described for fitting dihedral potentials in our paper. For each of the nine bonds and angles shown below, a total of ten iterations was sufficient to achieve self-consistent convergence. Below, we present all ten iterations for one bond, followed by the first and last iterations for the remaining interactions. In all cases, the energy levels plotted as a function of deviation of the bond or angle away from its optimal value (the minimum energy value) are plotted for only the respective bond or angle that is associated with the central PLA monomer in the trimer studied.

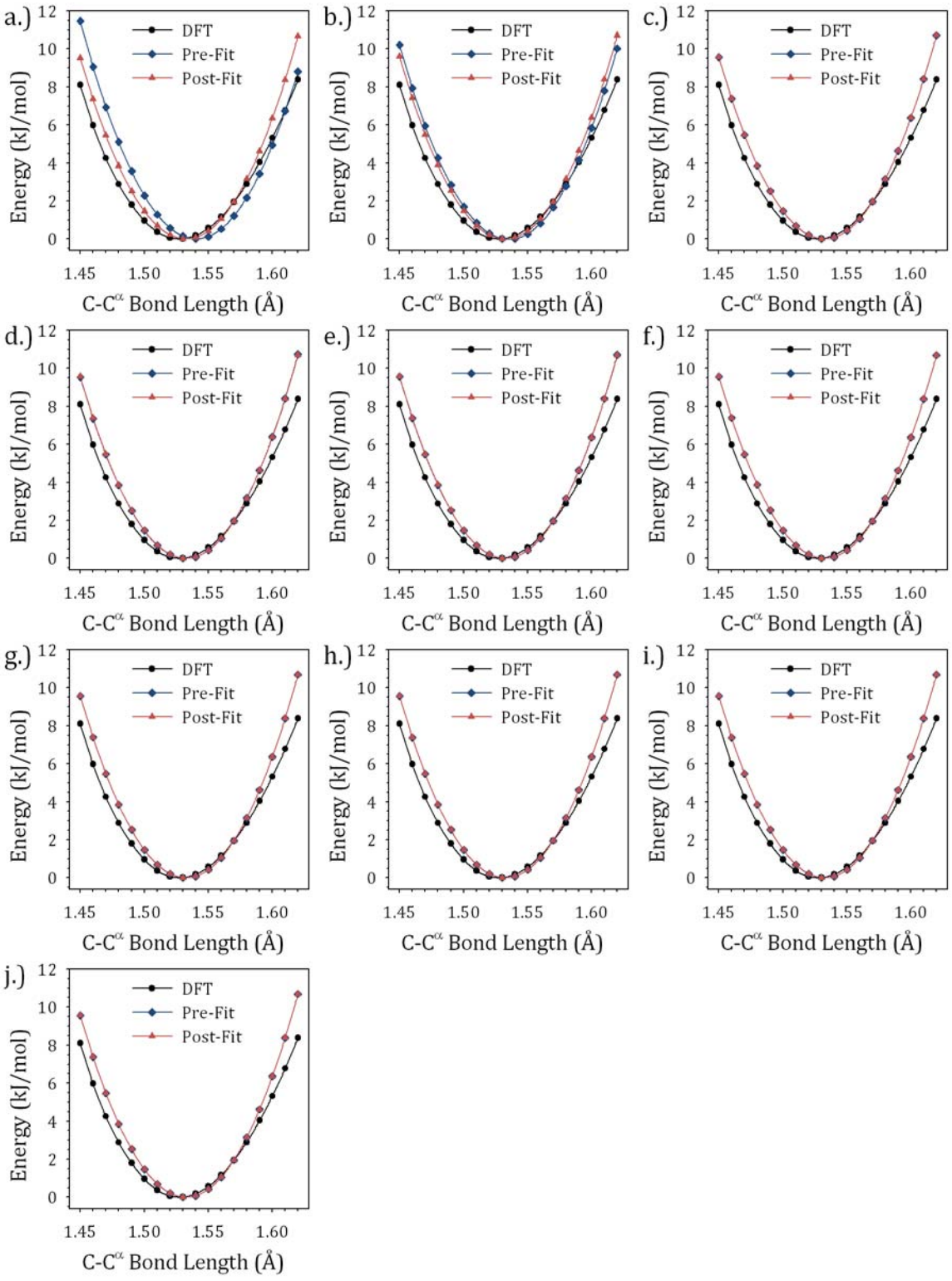

Figure 1. Self-consistent iterations for fitting the C-C$^{\alpha}$ bond parameters. Plots a–j correspond to ten self-consistent iterations. Pre-Fit and Post-Fit show energies before and after the least-squares fit. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted.

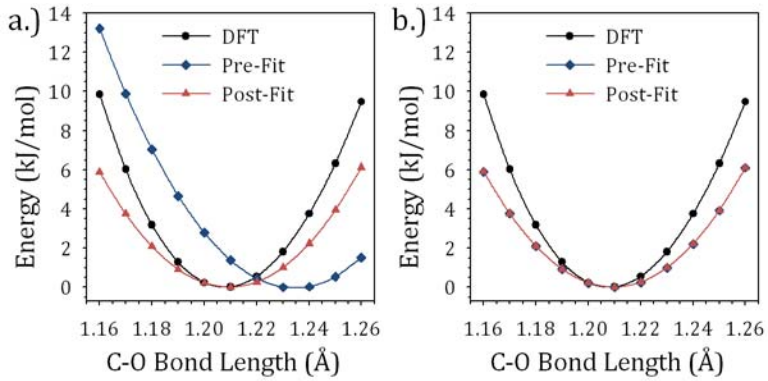

Figure 2. Self-consistent iterations for fitting the C-O bond. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

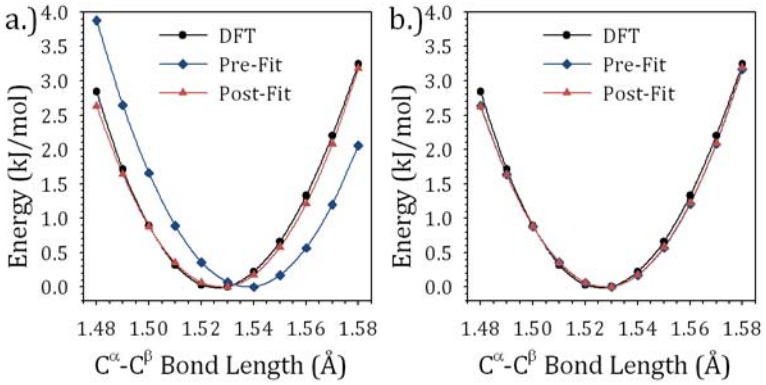

Figure 3. Self-consistent iterations for fitting the C^{α}-C^{β} bond. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

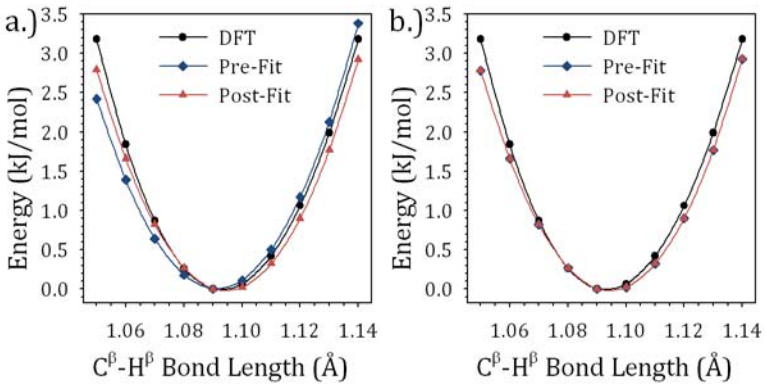

Figure 4. Self-consistent iterations for fitting the C^{β}-H^{β} bond. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

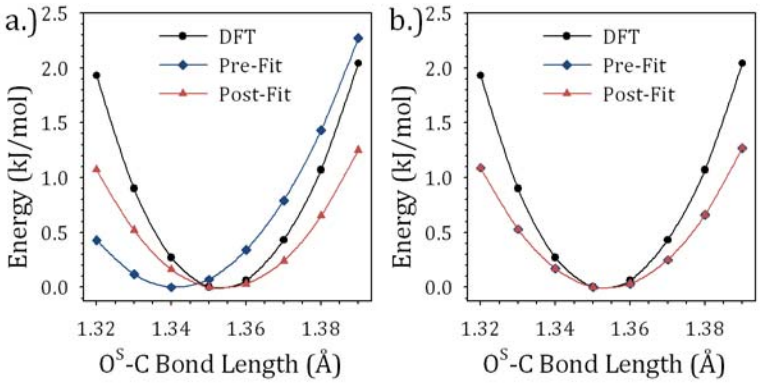

Figure 5. Self-consistent iterations for fitting the O^S-C bond. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

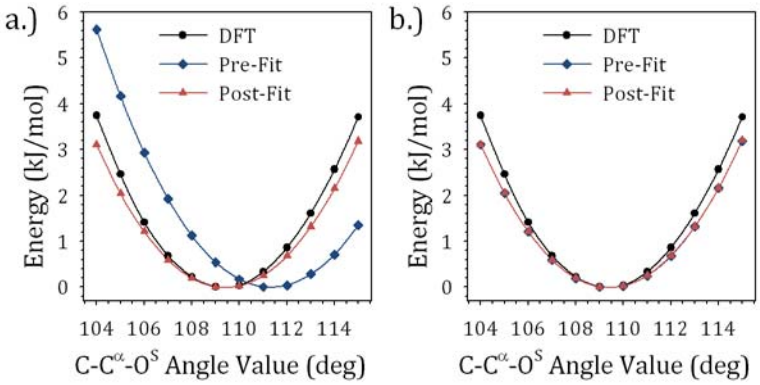

Figure 6. Self-consistent iterations for fitting the C-C^α bond. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

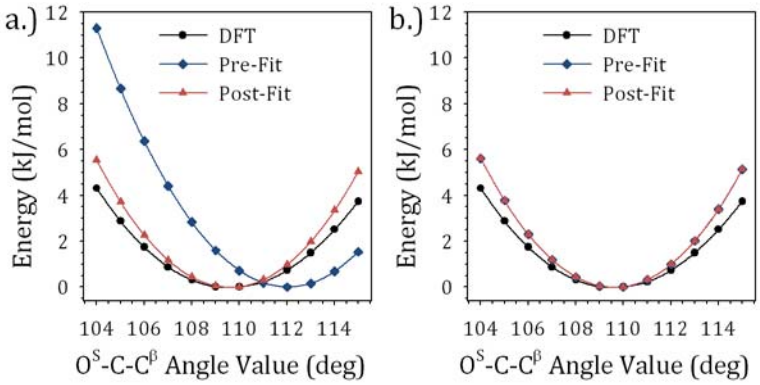

Figure 7. Self-consistent iterations for fitting the O^S-C-C^β bond angle. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

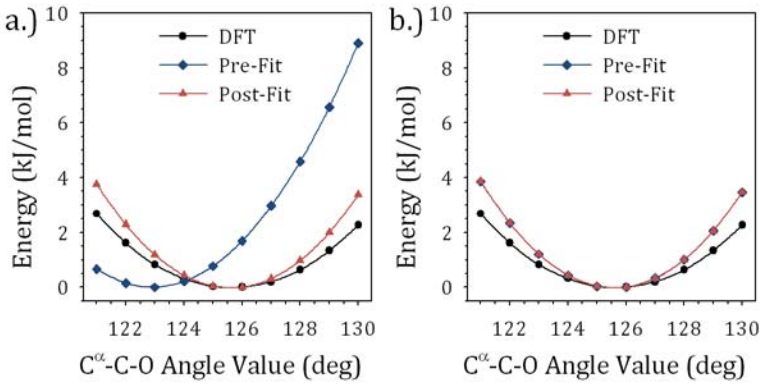

Figure 8. Self-consistent iterations for fitting the C^{α}-C-O bond angle. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

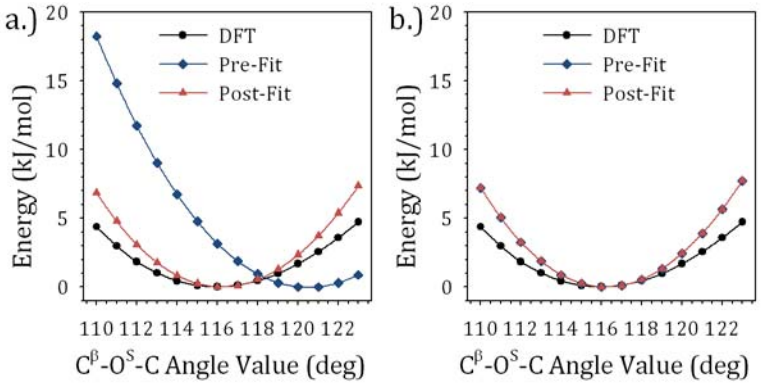

Figure 9. Self-consistent iterations for fitting the C^{β}-O^{S}-C bond angle. Between each iteration, the remaining bond and angle parameters listed in Tables 1 and 2 were adjusted. Plots a and b correspond to the first and tenth self-consistent iterations.

Table 1. Bond stretching parameters for the bonds adjusted in Figures 1 through 5. Force constants from OPLS were used in this work; initial bond lengths are from OPLS, and reported values for this work are after 10 self-consistent iterations. CHARMM parameters are shown for comparison.

	This Work	OPLS		CHARMM	
Bond	b_0 (Å)	b_0 (Å)	k_b (kJ/mol nm^2)	b_0 (Å)	k_b (kJ/mol nm^2)
C-C$^\alpha$	1.5109	1.5136	265265.6	1.522	167360
C-O	1.2017	1.2290	476976.0	1.220	627600
C$^\alpha$-C$^\beta$	1.5178	1.5290	224262.4	1.538	186190
C$^\beta$-H$^\beta$	1.0929	1.0900	284512.0	1.111	269450
O^S-C	1.3217	1.3270	179075.2	1.334	125520

Table 2. Angle bending parameters for the angles adjusted in Figures 6 through 9. Force constants from OPLS were used in this work; initial angle values are from OPLS, and reported values for this work are after 10 self-consistent iterations. CHARMM harmonic angle parameters are shown for comparison.

	This Work	OPLS		CHARMM	
Angle	θ_0 (deg)	θ_0 (deg)	k_θ (kJ/mol rad^2)	θ_0 (deg)	k_θ (kJ/mol rad^2)
C-C$^\alpha$-O^S	105.58	109.50	418.400	111.14	633.4576
C$^\alpha$-C-O	128.90	120.40	669.440	125.00	585.7600*
C$^\alpha$-O^S-C	108.84	116.90	694.544	109.60	334.7200*
O^S-C-C$^\alpha$	113.04	111.40	677.808	109.00	460.2400*

*These angle types have additional Urey-Bradley interactions