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A THz Vibrational Signature of Symmetry-breaking Structure of a Crystalline Polymer System

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[Introduction] Terahertz (THz) vibrational spectroscopy has provided a new experimental dimension for studying non-covalent interactions. Among many subjects that may attract a chemist's interest, one prominent is chirality. Non-covalent interactions are by nature electric force which has been known to conserve parity. Therefore, two enantiomorphous systems with different chirality should show the same vibrational spectra. However, for the racemic systems in which molecules or polymers with different chirality coexist, the conservation of chiral symmetry is not self-evident, and should be subjected to rigorous verifications whenever new experimental observations are available.

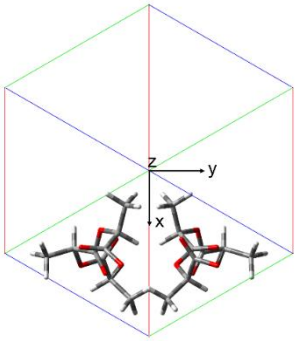

Figure 1 Packing conformation of scPLA within one primitive cell with *R3C* space group.

Poly(lactic acid) stereocomplex (scPLA), consisting of an equal amount of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), represents a typical racemic polymer system which can be relatively easily prepared with high crystallinity (larger than 70%).[1] Evidences in X-ray diffraction experiments have indicated that PLLA and PDLA adopt a lateral packing conformation in the crystalline regions of scPLA. Based on an assumption that PLLA and PDLA preserve a perfect chiral relation, and each of them adopt a 3_1-helical conformation, the crystalline regions of scPLA have been proposed to adopt *R3C* space group (Figure 1).[2,3] We have in this work optimized the crystal structure of scPLA by preserving and fully relaxing the *R3C* symmetric restriction, respectively. Through examining the reproduction of THz modes by the two sets of geometries, we will verify whether the *R3C* space group is a good symmetric restriction for scPLA, or in other words, whether the chiral symmetry is conserved.

[Experiment and simulations] A THz spectrum of scPLA was recorded by a THz time domain system (Aispec, Japan) at 78 K. Solid-state DFT simulations were performed in the CRYSTAL14 software package by complementing the periodic boundary condition. Based on the *R3C*-crystal structure of scPLA determined by the X-ray diffraction method, we performed geometry optimizations under the *R3C* and *P1* space groups, respectively. Note, in the *P1*-geometry optimization, all the symmetric restrictions on atomic coordinates were removed. The B3LYP-D* functional was used for both the *R3C*- and *P1*-simulations. For the *R3C* case, Gaussian's 6-311G(d,p) basis set was used; an integration grid in reciprocal space (6, 6) and an accurate control for bielectronic integral (8, 8, 8, 8 16) were employed. For the P1 case, Gaussian's 6-31G(d,p) basis set was employed concerning the significant increase of computational cost induced by reducing the

symmetric order; a smaller grid (3, 3) and a lower accuracy control (6, 6, 6, 6, 12) were used. All other computational parameters were used as the default values without specification. Frequency calculations were performed under the harmonic assumption. Infrared intensities were calculated through a periodic coupled-perturbed Hartree-Fock (CPHF) or Kohn-Sham (CPKS) analytical approach.

[Results and Discussion] The upper panel of Figure 2 shows the THz spectrum of scPLA; four bands have been resolved.[4] All the four bands show determinant polarizations (not shown); so they should originate exclusively from the crystalline regions of scPLA. The middle and bottom panels of Figure 2 show the IR-active normal modes reproduced with *R3C*- and *P1*-geometries, respectively. Clearly, the *R3C*-geometry predicts only three bands; while the *P1*-geometry reproduces all the four bands, whose assignments to experimental bands can be made unambiguously (it is worth noting that the discrepancy of frequency is mainly due to the ignorance of anharmonicity in simulation). This observation indicates that *R3C* space group is not a good symmetry restriction, and symmetry-breaking is an intrinsic property of the crystalline regions of scPLA.

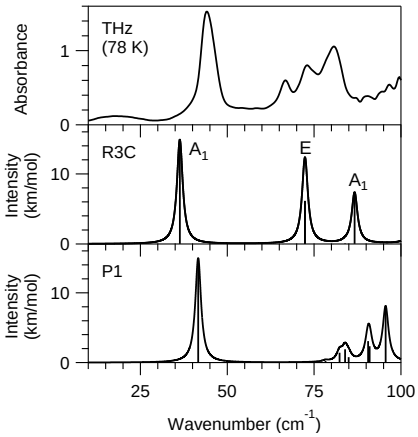

Figure 2 Comparison between a THz spectrum (bottom) of scPLA and IR-active normal modes simulated with *R3C* (middle) and *P1* (bottom) space groups. Lorentzian line shapes with a half-width at half-maximum=2.0 cm^{-1} are convolved into all simulated modes to provide a visual guide.

We first examine the violation of the 3_1-helical symmetry for PLLA and PDLA, as shown in Figure 3 (a) and (b), respectively. Compared with PLLA, PDLA exhibits a slightly stronger derivation from the 3_1-helical conformation. We then examine the structural disparity between PLLA and PDLA at the configuration and conformation levels, as shown in Figure 3 (c) and (d), respectively. The disparity is slightly larger at the conformational level than that at the configurational level, as a result of the imbalanced violation of the 3_1-helical symmetry between PLLA and PDLA.

The above analysis results implies that the solution of the Kohn-Sham function in the scPLA system does not conserve chiral symmetry, despite the non-covalent and covalent interactions conserve parity; therefore this observation should be regarded as an emerging phenomenon.[5] It is unclear whether this finding represents a special case of scPLA or it has general implications for other racemic polymer or molecular systems.

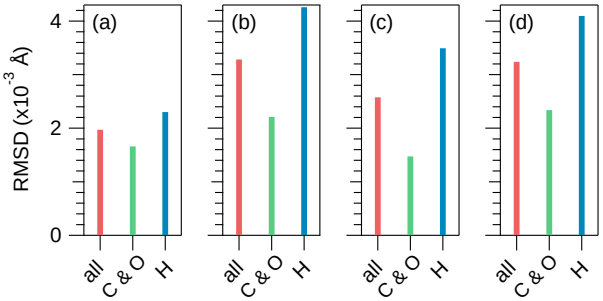

Figure 3 Evaluations of symmetry breaking for the *P1*-geometry of scPLA. Panel a and b examine the RMSD-violation of the 3_1-helical symmetry for PLLA and PDLA, respectively. Panel c and d examine the RMSD-structural-disparity for the constitutional and translational repeating units, respectively. RMSDs in each panel are examined with respect to all atoms, carbon and oxygen, and hydrogen, respectively.

Reference

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