Defects in Alpha and Gamma Nylon6: a Density Functional Tight Binding Study

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Nylon6 is a ubiquitous polymeric material known to most through its use in consumer products. In its pure form, nylon6 is a van der Waals bound crystal and can assume two configuration: alpha and gamma, which have similar cohesive energy. The alpha phase is believed to be more stable by 0.1-1.5 kcal/mol (per monomer). Real nylon6 presents a mixture of defected crystalline and amorphous phases, with the degree of crystallinity often reported to be of the order of 50%. While experimental studies observe semicrystalline nylon6, theoretical, and specifically, ab initio modeling has focused on pure crystalline phases. While the knowledge of the properties of pure crystalline phases of nylon6 is useful, there exist disconnect with the properties of real, defected and partially crystalline materials. Specifically to model defected nylon6, large simulation cells with thousands atoms are required (while unit cells of alpha and gamma nylon6 have ~10^2 atoms) which are impractical even with DFT. They can, however, be simulated with a near-DFT accuracy using Density Functional Tight Binding (DFTB).

Here, we present a comparative DFTB study of pure as well as defected alpha and gamma nylon6, including phononic contributions. We simulated different kinds of defects including single and several double vacancies, and interstitial strands. The defect formation energies for these types of defects are, respectively, 0.72/0.69, 1.41-1.52/1.31-1.41, and 1.66/2.581 kcal/mol per monomer for single, double vacancies, and interstitials, in alpha/gamma phases. Interstitials will therefore be induced at room temperature, and even if pure phases were to be synthesized they are likely to become highly defective.

We find that phononic contributions and defects to not significantly change the relative phase stability of the two phases.

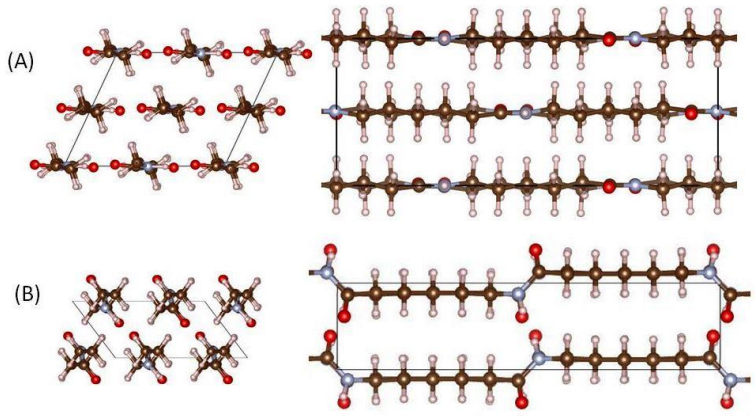

Figure 1. *Crystal structures of alpha (A) and gamma (B) nylon6.*