Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Rydberg transitions as a probe for structural changes and phase transition at polymer surface. ATR-FUV-DUV and quantum chemical study of poly(3-hydroxybutyrate) and its nanocomposite with graphene

Supporting Information

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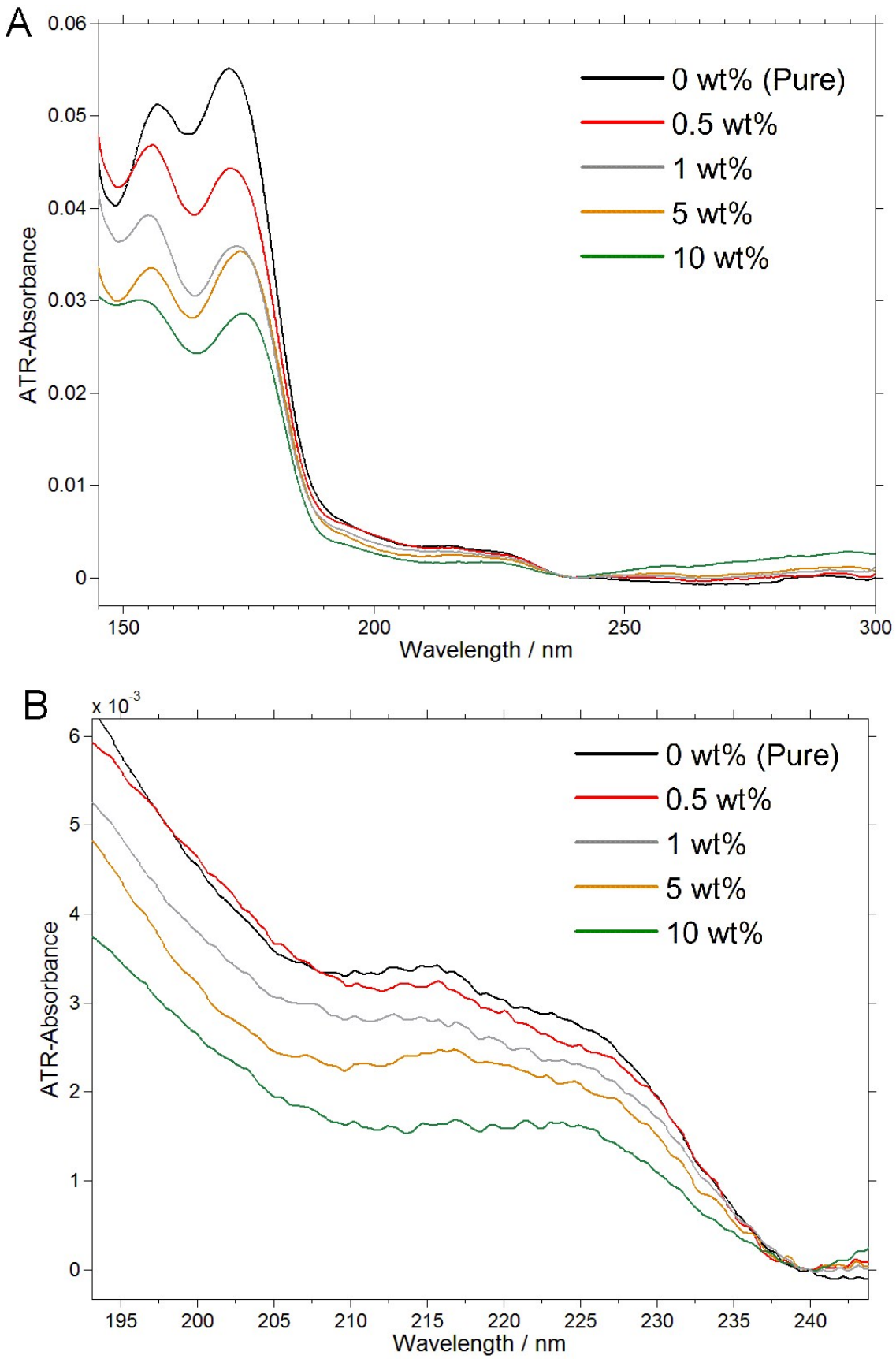

Figure S 1. The experimental ATR-FUV-DUV spectra of PHB and PHB-graphene nanocomposites. The spectra were smoothed (Savitzky-Golay algorithm, 151 data-points/0.01 nm) and vertical offset was performed at 240 nm.

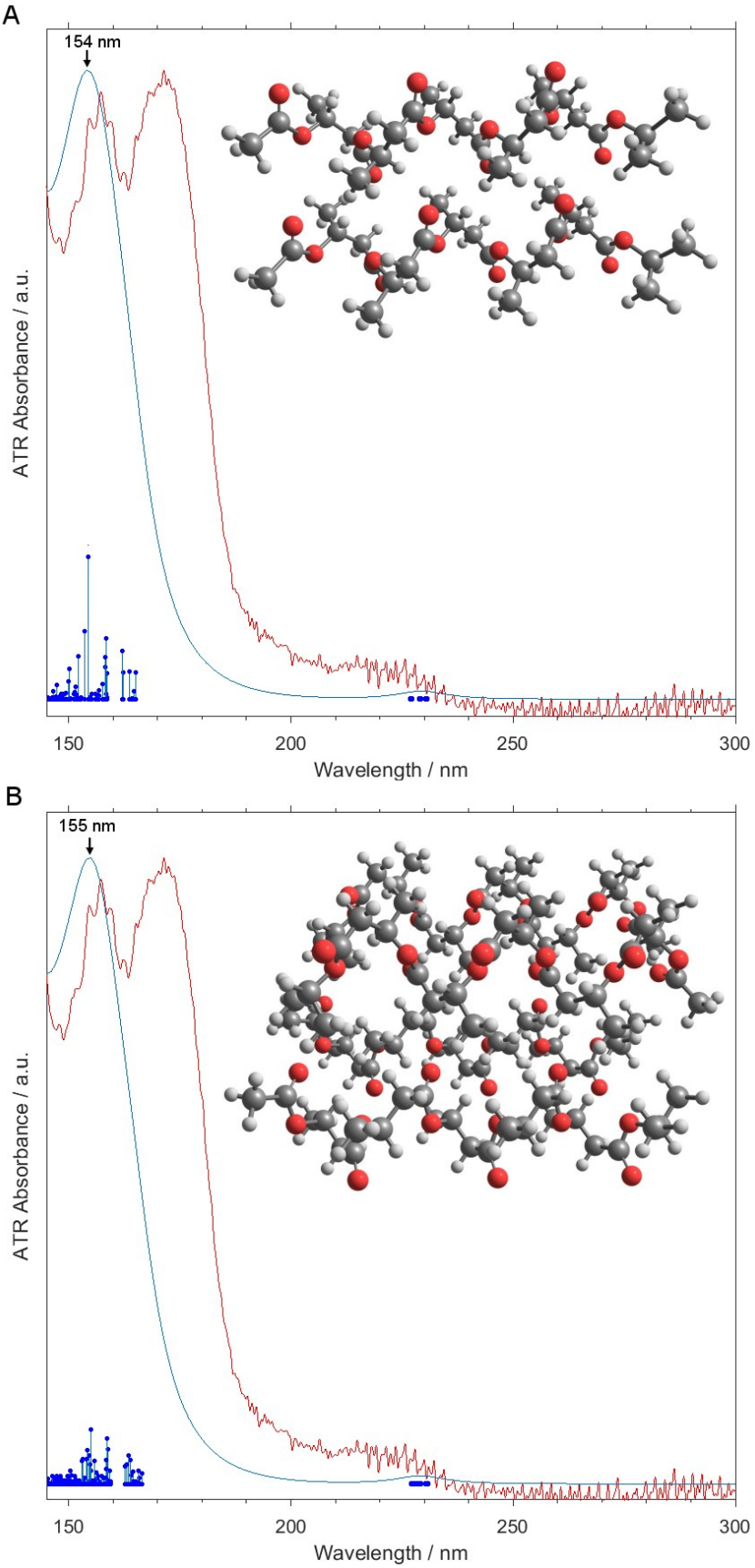

Figure S 2. A comparison between the more complex models of α-crystalline PHB based on TD-CAM-B3LYP/6-31G calculations; (A) a two-chains model (12 units); (B) a four-chains model (24 units).

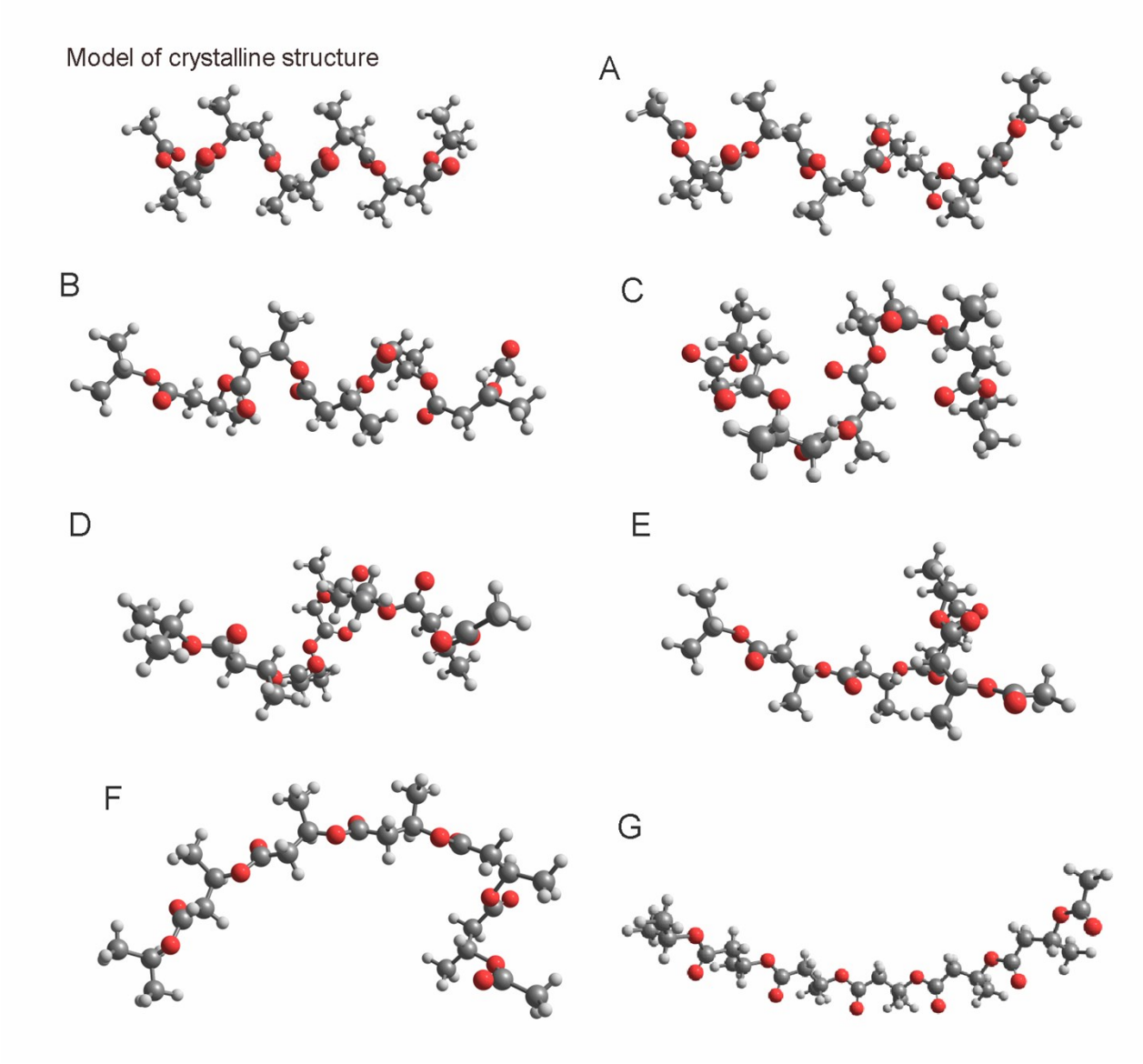

Figure S 3. The models of amorphous PHB considered in the present study. Model of the crystalline structure (the starting point of the scan) and the structures A-G which are local minima approximating possible amorphous stat of the polymer chain. These structures follow the pattern of forced unfolding of the helix of the crystalline model, induced by an increase of the model length (as described in the min article). The potential structures resolved in a relaxed scan at B3LYP/6-31G(d,p) level were afterwards reoptimized at B3LYP/cc-pVTZ level, thus resulting with different levels of recurrent folding of the polymer chain.

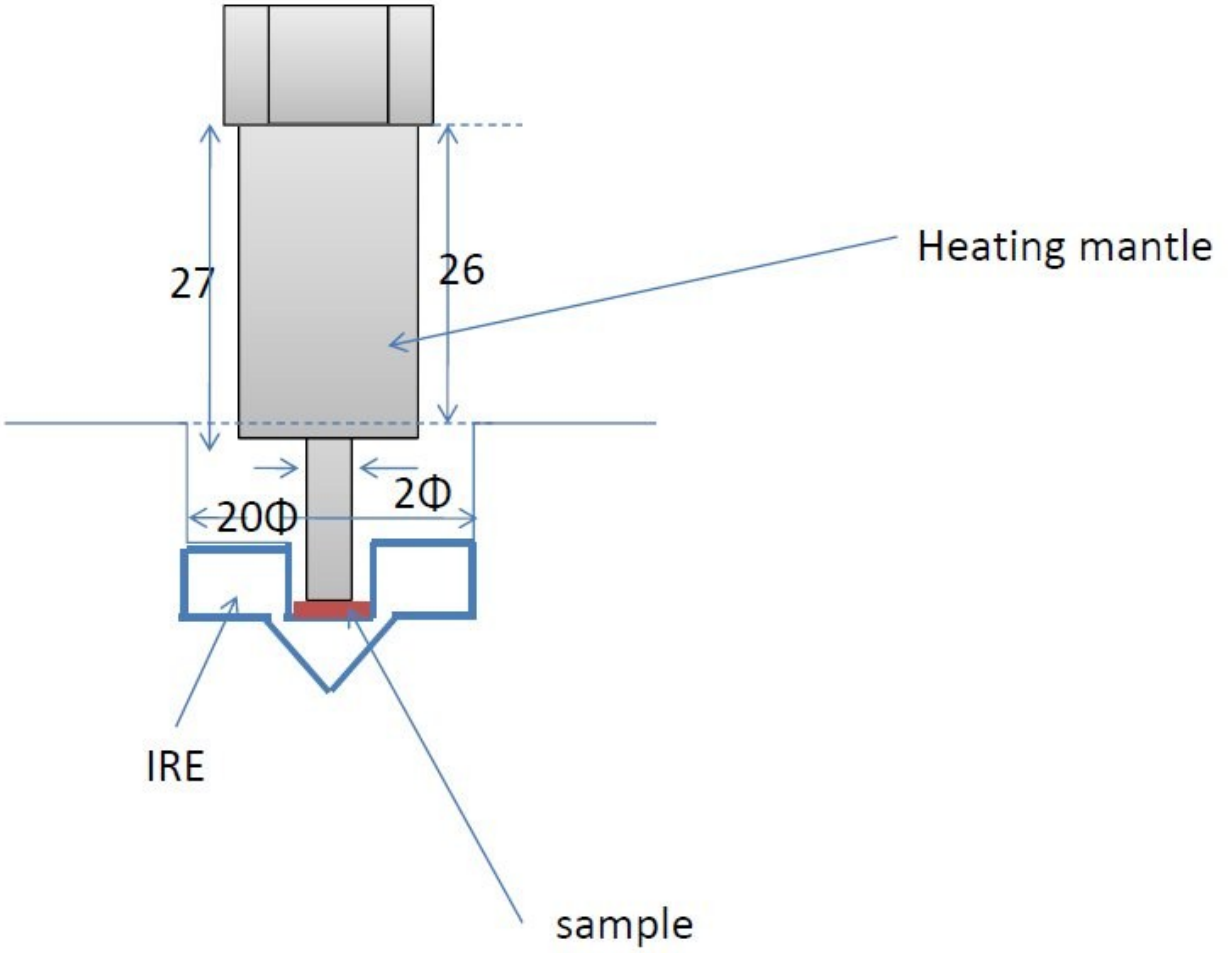

Figure S 4. The scheme of the temperature control assembly used in the measurements of the temperature-dependent spectra of pure PHB

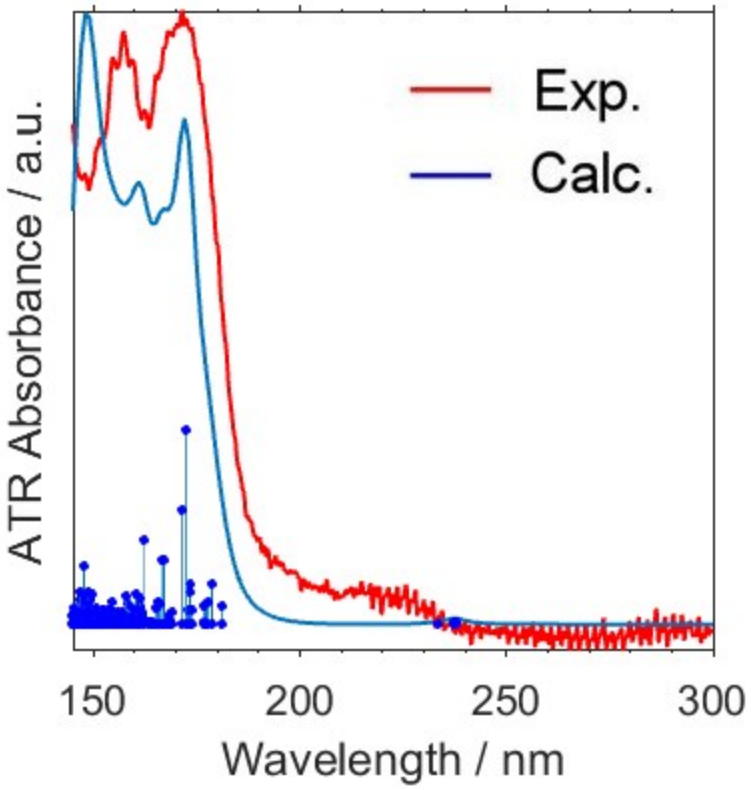

Figure S 5. Simulated (TD-CAM-B3LYP/aug-cc-pVDZ) FUV-DUV spectrum of α-crystalline PHB based on a 6-unit single chain model compared with the experimental spectrum of PHB. In the simulated spectrum lower bandwidth was applied and additionally a linear scaling of the wavelength axis by ~10 nm was performed so that the calculated peak at 171 nm (A_{max}) matches the position of the experimental one.

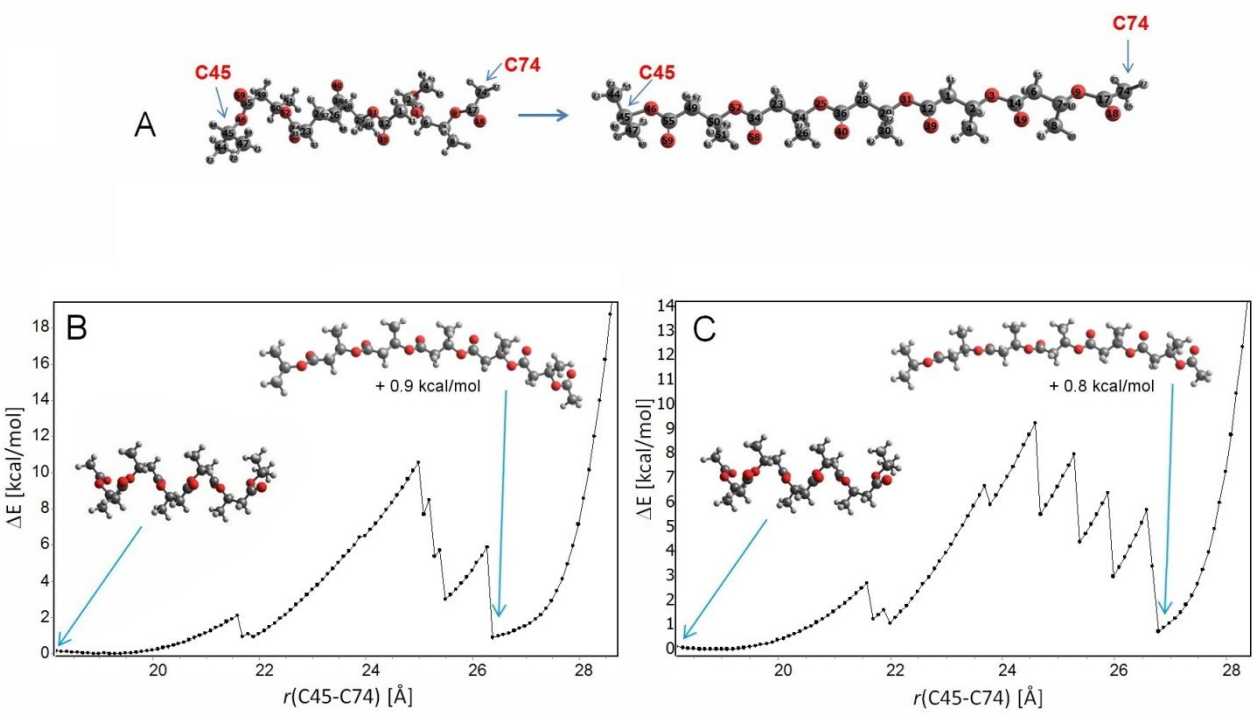

Figure S 6. Results of relaxed scan of PHB model in search for amorphous states, repeated at higher level of theory as suggested during peer-revision. The scan coordinate was the distance between C45 and C74 atoms (A); plots of the scanned potential energy at B3LYP/6-31++G(d,p) (B) and B3LYP/6-311G(d,p) (C) levels. These results confirm the previous conclusions from B3LYP/6-31G(d,p) scan (Fig. 6 in the main article).