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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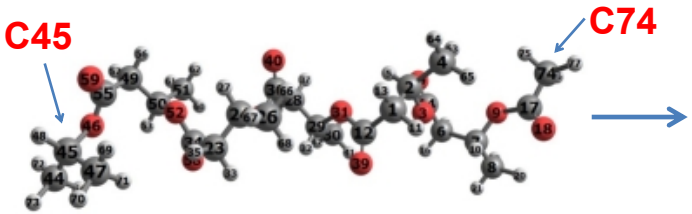
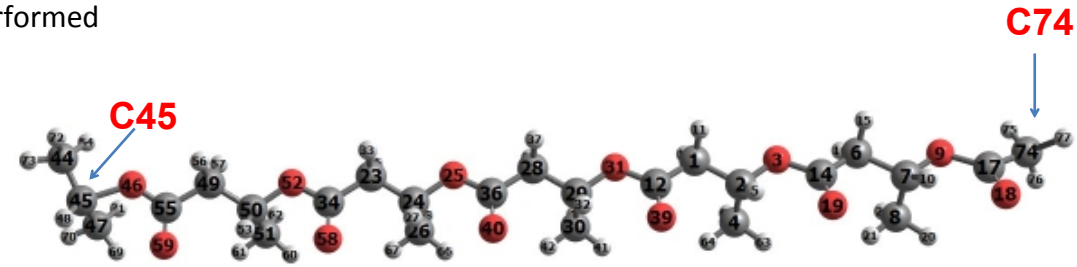
A systematic approach for approximation of amorphous polymer

- **scan** of the potential energy vs. variable chain length **[steps: 0.1 Å]**
- chain length dictated by the distance between terminal atoms **C45** and **C74**
- at each step **geometry optimization** is being performed

First approximation – semi-empirical PM7 method

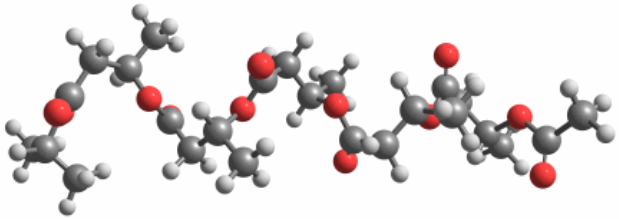


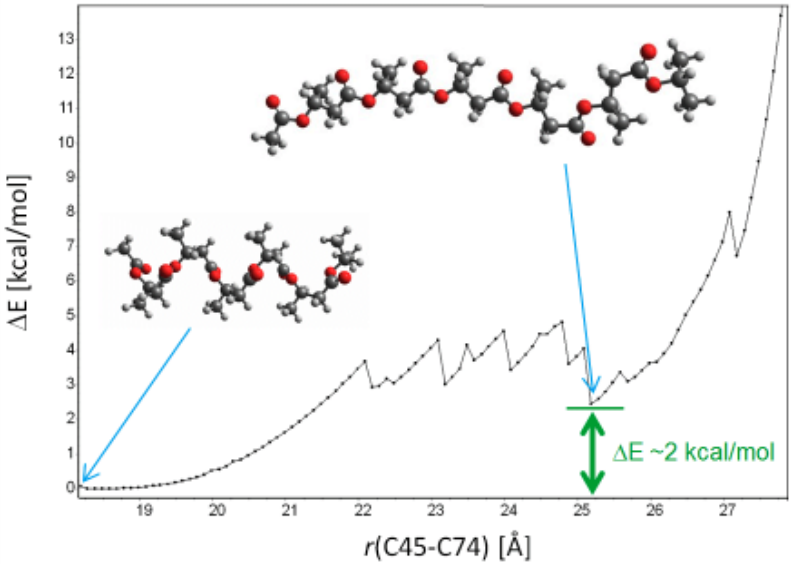
Start point – single-chain model of crystalline PHB



Start point – single-chain model of crystalline PHB

Animation:

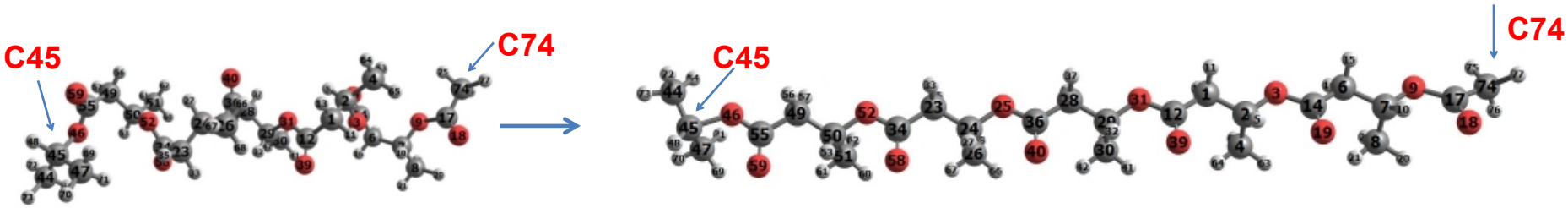




A systematic approach for approximation of amorphous polymer

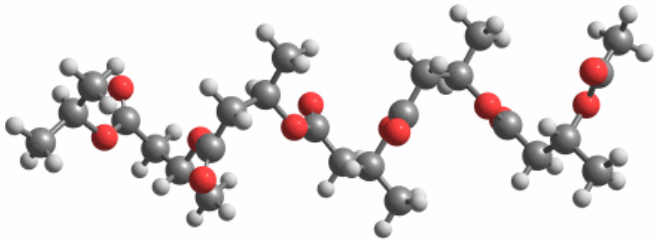
More accurate approximation
DFT-B3LYP/6-31G(d,p)

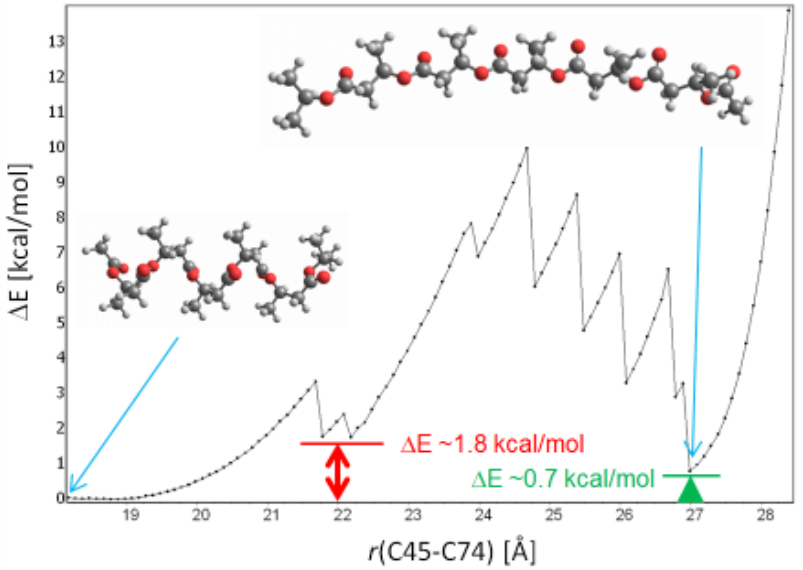
- **relaxed scan DFT-B3LYP/6-31G(d,p) using the validated principle**
- DFT scan **fully confirmed** the approximated results and even brought **more insightful conclusions**



Start point –
single-chain model of crystalline PHB

Animation:





Unfolding of PHB helix – projection along chain axis