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INSIGHT ON RELATIONSHIP BETWEEN CRYSTALLINITY AND BAND GAP ENERGIES OF POLYHYDROXYALKANOATES POLYMERS

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Introduction

Polyhydroxyalkanoates (PHAs) have emerged as biocompatible and bioresorbable polymers, gaining prominence in diverse applications like agriculture, pharmacology, and biomedicine due to their eco-friendly nature [1]. These naturally occurring polymers, produced by bacteria, form homo- or copolymers and are studied for film production due to their resistance to UV radiation and thermoplastic properties. Variations in monomer composition in PHAs, such as short-chain-length (scl-PHAs) and medium-chain-length (mcl-PHAs), enable customization of film properties, finding applications in packaging and biomedical fields [2]. However, challenges like high production costs, brittleness, and variable degradation rates persist. This article explores the application of density functional theory (DFT) for studying PHA polymers' electronic structure, addressing challenges like the size and complexity of polymer systems and conformational flexibility [3]. The study aims to enhance DFT accuracy through improved treatment of weak intermolecular interactions and advanced functionals, contributing significantly to polymer science and technology.

Methodology

The study explores (PHAs) synthesis using the Cupriavidus necator B-10646 strain for high-yield copolymer production, employing various carbon sources and Schlegel medium. The synthesized PHAs are characterized using methods like FTIR spectroscopy, X-ray diffraction, and UV-spectroscopy, focusing on chemical composition, crystallinity, and optical properties. Density Functional Theory (DFT) calculations are conducted on PHA oligomers to optimize geometry and analyze electronic structures, using ORCA 5.0.3 and r2SCAN-3c methods under vacuum and CPCM conditions. The study investigates band gaps in PHAs, comparing DFT results with experimental data to establish correlations, especially focusing on the impact of crystallinity on electronic properties. Notably, a consistent band gap is observed in polymers with 6 monomers, with further analysis indicating a stabilization in band gap energies at 10 monomers, highlighting the influence of monomer composition and solvent interactions on the electronic structure of PHAs.

Conclusion

Our research on polyhydroxyalkanoates (PHAs) uncovers a critical relationship between crystallinity and band gap energy, with a notable plateau indicating a threshold in PHA electronic properties. This discovery is vital for achieving consistent electronic behavior in applications. The observed strong negative correlation between crystallinity and band gap, evident in both vacuum and CPCM conditions, is crucial for designing PHAs for electronic and optoelectronic uses. Integrating computational methods with experimental data, our study significantly advances polymer science, paving the way for sustainable, tailored PHA materials in technology.

References:

1. A. Baptista-Perianes, S.M. Malmonge, M.M.O. Simbara, A.R. Santos Junior, In vitro Evaluation of PHBV/PCL Blends for Bone Tissue Engineering, Materials Research 22 (2019). https://doi.org/10.1590/1980-5373-mr-2019-0338.
2. S.-P. Lim, S.-N. Gan, I.K.P. Tan, Degradation of medium-chain-length polyhydroxyalkanoates in tropical forest and mangrove soils, Appl Biochem Biotechnol 126 (2005) 23–33. https://doi.org/10.1007/s12010-005-0003-7.
3. J.T. Orasugh, S.S. Ray, Prospect of DFT Utilization in Polymer-Graphene Composites for Electromagnetic Interference Shielding Application: A Review, Polymers (Basel) 14 (2022) 704. https://doi.org/10.3390/polym14040704