

High-energy electronic transitions of polymer-graphene type nanocomposites. Attenuated total reflection far/deep -ultraviolet spectroscopy and DFT study of poly(3-hydroxybutyrate)-graphene nanocomposite material

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[Abstract] We explore high-energy electronic properties of poly(3-hydroxybutyrate) or PHB and its graphene-based nanocomposite in solid state by attenuated total reflection far/deep-ultraviolet (ATR-FUV-DUV) spectroscopy (145-300 nm) and quantum mechanical study based on time-dependent density functional theory (TD-DFT) and periodic DFT calculations. The major FUV absorption in the region of 150-170 nm of PHB is due to π -Rydberg 3p orbitals and weak band near 227 nm arises mainly from π to π^* transitions. We observe spectral variations in the major FUV absorption peak of PHB due to temperature changes and upon the formation of nanocomposite with graphene.

[Introduction] Attenuated total reflection far/deep-ultraviolet (ATR-FUV-DUV) spectroscopy has been recently developed in our group [1,2]. The major advantage of ATR-FUV-DUV spectroscopy is the capability of convenient spectral measurements in the region 145-300 nm; 8.55-4.13 eV of wide range of samples in condensed phase. So far we have succeeded in examining a wide range of samples, i.e. water and aqueous solutions, semi-conductors, ionic liquids, and a variety of organic molecules [2-6]. Preliminary insights into high-energy electronic transitions of polymers, including the details of Rydberg orbitals have been obtained in the study of nylons [3]. In the present work we investigate the structure and intermolecular interactions in poly(3-hydroxybutyrate) (PHB) by ATR-FUV-DUV with an interpretation of experimental data by quantum mechanical study. PHB is a semi-crystalline, biodegradable polymer characterized by specific intermolecular interaction, weak C-H \cdots O=C hydrogen bonds, strongly affecting its structure and properties. The classic UV spectroscopy is not feasible for structural investigations of polymers; their UV (380-300 nm) and DUV absorption is rather insignificant. Instead, the major UV absorption peaks of polymers are located in the FUV region and are related to Rydberg transitions. Due to the shape of Rydberg orbitals, the corresponding high-energy electronic transitions of polymers are very sensitive to their structural changes. We focus on the FUV-DUV spectral variations due to structural changes of PHB upon the thermally induced expansion and upon the formation of a nanocomposite with graphene. A quantum chemical model of thermally expanded polymer crystal lattice provides hints into the spectral variations. It may be also concluded that the crystallinity of PHB is affected by the increasing content of graphene in the nanocomposite.

[Methods] The details of ATR-FUV-DUV spectrometer have been reported earlier [1,2]. It uses an internal reflective element (IRE) made of sapphire (~8 mm of path length, UV grade, Opto-line, Tokyo) and a 30 W deuterium lamp as a light source. The angle of beam incidence is 70°. During the measurements the interior of the spectrometer is continuously purged by

dry nitrogen flow ($3 \text{ dm}^3 \text{ min}^{-1}$). However, the sample is conveniently contained in the open air and only a proper contact surface with the prism element needs to be maintained. The spectrometer operates in the wavelength region of 145–300 nm (8.55–4.13 eV).

Quantum chemical study is based on periodic DFT (Crystal 09 code; B3LYP/TZVP level) and time-dependent density functional theory (TD-DFT; Gaussian 09E; CAM-B3LYP/aug-cc-pVDZ and CAM-B3LYP/6-31+G* levels) calculations. Periodic DFT is used for the calculations of total density of states (TDOS) of crystalline PHB, and the simulation of lattice expansion by optimization of the polymer geometry (atoms only; fixed lattice vectors). TD-DFT is used for the calculation of vertical transition energies and corresponding oscillator strengths and determination of the relevant molecular orbitals (MOs). Crystalline structure of PHB is used as the basis for periodic DFT; extracted models of increasing complexity are used as the basis for TD-DFT calculations.

[Results and Discussion] The FUV-DUV spectrum of PHB is explained by the quantum chemical calculations. The absorption near 150–170 nm is related to multiple transitions with the most relevant ones involving excitation from π orbitals to Rydberg 3p orbitals. The low-intensity peak near 227 nm is due to weak π to π^* transitions. The shape of Rydberg orbitals make them sensitive to the structure of the polymer, which allow to study the structural changes of PHB occurring during the thermal expansion and upon the formation of a nanocomposite with graphene. The results based on TDOS calculation, simulation of the lattice expansion and TD-DFT calculations for the more complex polymer models provide insights into the structural changes of PHB polymer.

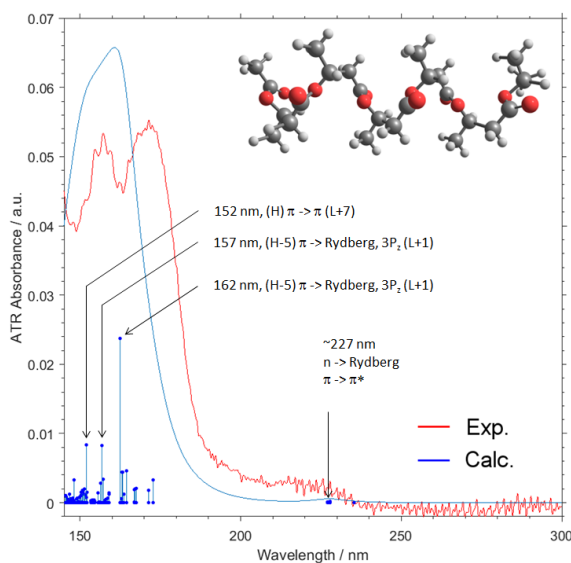


Fig. 1. Simulated (TD-CAM-B3LYP/aug-cc-pVDZ) FUV-DUV spectrum of α -crystalline PHB based on 6 units single chain model compared with the experimental spectrum of PHB.

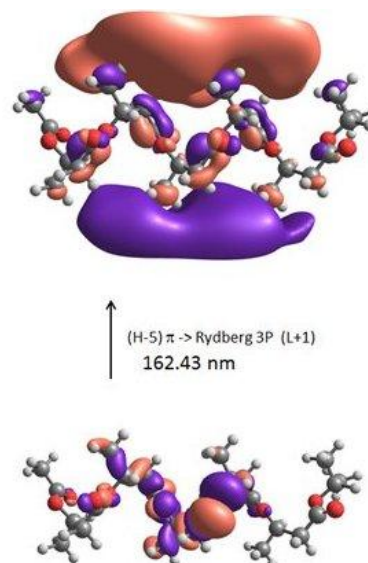


Fig. 2. The most relevant MOs for the major FUV transition of α -crystalline PHB (TD-CAM-B3LYP/aug-cc-pVDZ).

[References]

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