A revisitation of the polymorphism of poly(butylene-2,6-naphthalate) from periodic first-principles calculations

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ABSTRACT

Periodic density functional theory calculations are here used to investigate polymorphism in poly(-butylene-2,6-naphthalate) (PBN) and to understand the intra- and inter-molecular effects which are responsible for its behavior. Despite its similarity to poly(butylene terephthalate), the larger π-electron conjugation promoted by the presence of naphtyl rings generates peculiar intramolecular effects and stronger interchain packing interactions which cause some differences between the two polymers. This is particularly evident by comparing the structural and spectroscopic data predicted for the α and β crystals with respect to the respective one dimensional infinite chain models. Two different interpretations have been proposed in the previous literature to describe the structural transitions from the α to the β polymorph of PBN upon mechanical deformation or thermal treatments: from one hand, the setting on of a transplanar conformation on the methylene chains has been proposed while, on the other hand, a larger coplanarity of the ester groups and the naphtyl rings has been suggested. Our calculations reveal that both these effects are present in β-PBN and should be both taken into account to give an interpretation of the trends observed by IR spectroscopy and structural characterization.

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1. Introduction

The family of aromatic polyesters comprises some polymers, such as poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT), whose technological importance is now well-assessed in many different fields. However, other members of this class are engendering more and more interest both for their properties and possible applications but also for their peculiar physicochemical behavior. In this context, poly(butylene-2,6-naphthalate) (PBN) has been the focus of a few studies [1—13], aimed at understanding its molecular structure, also in view of the interpretation of its excellent thermal and mechanical properties. Indeed, PBN proved to be a good candidate as an innovative engineering plastics, thanks in particular to its thermostability, hydrolytic stability and gas barrier properties. As in the case of other polymers and molecular materials, the desired properties are intimately related to the structure developed upon processing (e.g. temperature treatments, mechanical deformation etc.) and polymorphism effects are key phenomena in this context. The knowledge of the behavior of the polymer at a molecular scale is therefore mandatory for the explanation of its structure-property correlations.

PBN is a semicrystalline polymer and two crystal modifications, α and β, have been reported by Watanabe [1] and Koyano et al. [2]:α-PBN appears under normal condition while a transition to β-PBN is observed under mechanical stretching, similarly to PBT [14—29]. In further papers [3,4,6], it has been reported that β-PBN can be also generated by isothermal/non-isothermal crystallization at high temperature or under pressure; moreover, the presence of mesophases has been detected and investigated [9,10]. All these studies agree in pointing out the significant supramolecular effects that characterize this polymer and which are generated by strong interchain interactions between naphthalene groups, responsible for its polymorphism and its complex crystallization/melting process. Different characterization techniques have been adopted in these works, including X-ray diffraction (XRD) [1—4,6,8], infrared (IR) spectroscopy [3,4,8] and Nuclear Magnetic Resonance (NMR) [11,13], but different interpretations have been proposed to explain the polymorphic transitions found in PBN.

Based on the similarity between PBN and PBT, some authors [3,8,11] described the transition from the α to the β phase in terms of a conformational transition leading to a transplanar structure on the ester group and on the methylene chain, as indeed found for PBT; on the other hand, other authors [4,13] discarded this interpretation but described the β phase as a structure where the polymer chains are characterized by a larger degree of coplanarity

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of the ester groups and the naphtyl rings, while the conformation on the methylene chain is the same (all-trans) in both α- and β-PBN. The experimental results do not help in unraveling these discrepancies since there are evidences supporting both these interpretations. Therefore the understanding of the polymorphism properties of PBN is still incomplete and unclear, even if it would be a preliminary and mandatory step for the rationalization of the structure-dependent physicochemical properties of these systems.

The present work aims at giving a contribution in this ground, shedding light on the polymorphism behavior of PBN polymorphs by adopting state-of-the-art molecular simulations techniques seldom adopted before and that possess an high predictive power. Indeed, in previous papers [29–33], we demonstrated that first-principles computational techniques can give a detailed description of both the structural and vibrational properties of the crystal phase in semicrystalline polymers, allowing to find an answer to the ambiguities and the debated interpretations proposed by different authors. In this context, our most recent works focused on aromatic polyesters: we presented indeed a computational approach based on periodic Density Functional Theory (DFT) calculations augmented with an empirical dispersion correction (DFT-D) [34–36] for the spectroscopic characterization of poly(trimethylene terephthalate) [30] (PTT) and for the investigation of the polymorphic behavior of PBT [29]. The CRYSTAL09 code [37,38] has been used to this aim: this program has indeed been applied successfully to many other polymeric systems (polystyrene [39,40], polyglycine [41], nylon 6 polymorphs [31], nylon 6,6 [32], polytetrafluoroethylene [33]) and proved to be a powerful tool for the theoretical characterization of the crystal domains of semicrystalline polymers.

Based on these results, the same methodology used for PBT [29] will be here applied to PBN, to investigate its polymorphic behavior on the basis of the crystal/molecular structure and of the vibrational (IR) spectra predicted by the calculations.

2. Computational details

Full geometry optimization of the crystal structure and chain conformation and the calculation of the IR spectra of PBN have been carried out by means of the CRYSTAL09 code [37,38] in the framework of Density Functional Theory. Based on previous computational investigations of polymer systems [29–33,39–41], we adopted the B3LYP [42,43] hybrid exchange-correlation functional with the 6-31G(d,p) basis set, introducing the empirical correction for dispersion interaction (B3LYP-D) proposed by Grimme [34–36] (related parameters are taken from Ref. [29]). This choice gave indeed a very good description of both the structure and the vibrational spectra. In all calculations, the atomic positions and the lattice parameters were fully optimized: as first guess input structures for the two α and β polymorphs we used the cartesian coordinates and cell parameters reported by Koyano et al. [2].

In addition to the simulations of the crystals, we carried out also simulations for infinite one dimensional polymer chains (1D model chains): in this case CRYSTAL09 allows to build automatically a polymer system by applying periodic boundary conditions in the chain axis direction (c cell parameter) while fixing a and b parameters to 500 Å in order to describe an isolated infinite chain. In particular, we considered as starting geometries three structures, having respectively the conformations observed in α and β crystals (experimental geometries [2]) and the all-trans conformation. In these cases, a chain repeat distance (c') which is the double of the related c crystal cell parameter has been chosen: indeed the use of periodic boundary conditions in chain axis direction might impose unphysical constraints on the conformational angles; this problem gradually disappears if larger supercells are used. In our case,

adopting a repeat distance of the same order of the c parameter already gives the same description of the conformation of the chains but we preferred to adopt a larger value as a best compromise for a more reliable description of conformational effects. The optimized structures of all these crystals and 1D model chains are sketched in Fig. 1.

In all cases, normal frequencies calculation at Γ point has been carried out on the optimized geometries as achieved by diagonalization of the (numerically calculated) Hessian matrix.

The DFT-D computed spectra have been compared with the experimental IR spectra reported by Chiba et al. [3] and Ju et al. [4]. To compare the computed and the experimental data, the calculated frequencies were scaled by 0.9665: this scaling factor has been determined to put the reference band computed at 1777.5 cm^{-1} (C=O stretching band) for the α crystal in correspondence to the band found at 1718 cm^{-1} in the experimental spectra [4].

It should be not noted that, by definition, our calculations provide a reliable description of the crystal domains and of regular chain conformations (1D model chain) of polymers but obviously they do not take into account the existence of the amorphous domains. Therefore, in the comparison with the experimental spectra or with other structural data, we need to bear in mind that the real nature of semicrystalline polymers is only partially described by the computational approach here adopted.

3. Results

3.1. Structure and conformation of PBN polymorphs

In Table 1 the numerical values of the cell parameters and torsional angles predicted by DFT-D calculations for the α and β polymorphs are reported and they are compared to the experimental data found by Koyano et al. [2].

It is evident that for both forms non negligible differences are found, indicating that the DFT computed structures do not follow the proposed experimental ones. This is evident if the torsional angles associated to the ester groups and to the methylene chains are analyzed: Koyano et al. [2] proposed indeed a S′G′TGS conformation for the α form and a more extended TSTS′T conformation for the β form. These values parallel those found by Yokouchi et al. [14] for PBT (α: G′G′TGG, β: TSTS′T), apparently indicating that polymorphism effects are similar for both polymers. By inspection of the computed torsional angles we find that the S′GTGS conformation is not stable in the α crystal: indeed the S angle (123°) observed experimentally is relaxed in an almost transplanar value (161°) by the calculations, predicting an approximate TGTG′T conformation for the α polymorph. On the other hand the S angle in β-PBN (106°) relaxes in a G angle (66°) after full geometry optimization, resulting also in this case in a TGTG′T conformation. As discussed above, the experimental structures proposed in Ref. [2] are similar to those reported for PBT in Ref. [14]: however while for α-PBT a general agreement was found among different authors [29], β-PBT has been found to possess a transplanar conformation, contrary to the TSTS′T conformation proposed in Ref. [14]. Therefore, we could expect that also for PBN, similar discrepancies could be present, justifying the difference between experimental and DFT computed parameters. Indeed, in our previous paper [29], we adopted the same computational approach to study PBT polymorphs, starting from the experimental geometries proposed by Yokouchi et al. [14]: for β-PBT (called β* in Ref. [29]) a TGTG′T conformation was found instead of a TSTS′T conformation, exactly as in the case of β-PBN. On the other hand, for α-PBT a GGTG′G′ was found to be stable, in agreement with the experiment. The fact that in PBN neither the GGTG′G′ conformation nor the proposed S′G′TGS are obtained after