

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

Alberto Milani

Politecnico di Milano – Dip. Chimica, Materiali, Ing. Chimica “G. Natta”, P.zza Leonardo da Vinci 32, 20133 Milan, Italy

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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

E-mail address: alberto.milani@polimi.it.

of the ester groups and the naphthyl 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], polytetrafluorethylene [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'GTGS are obtained after

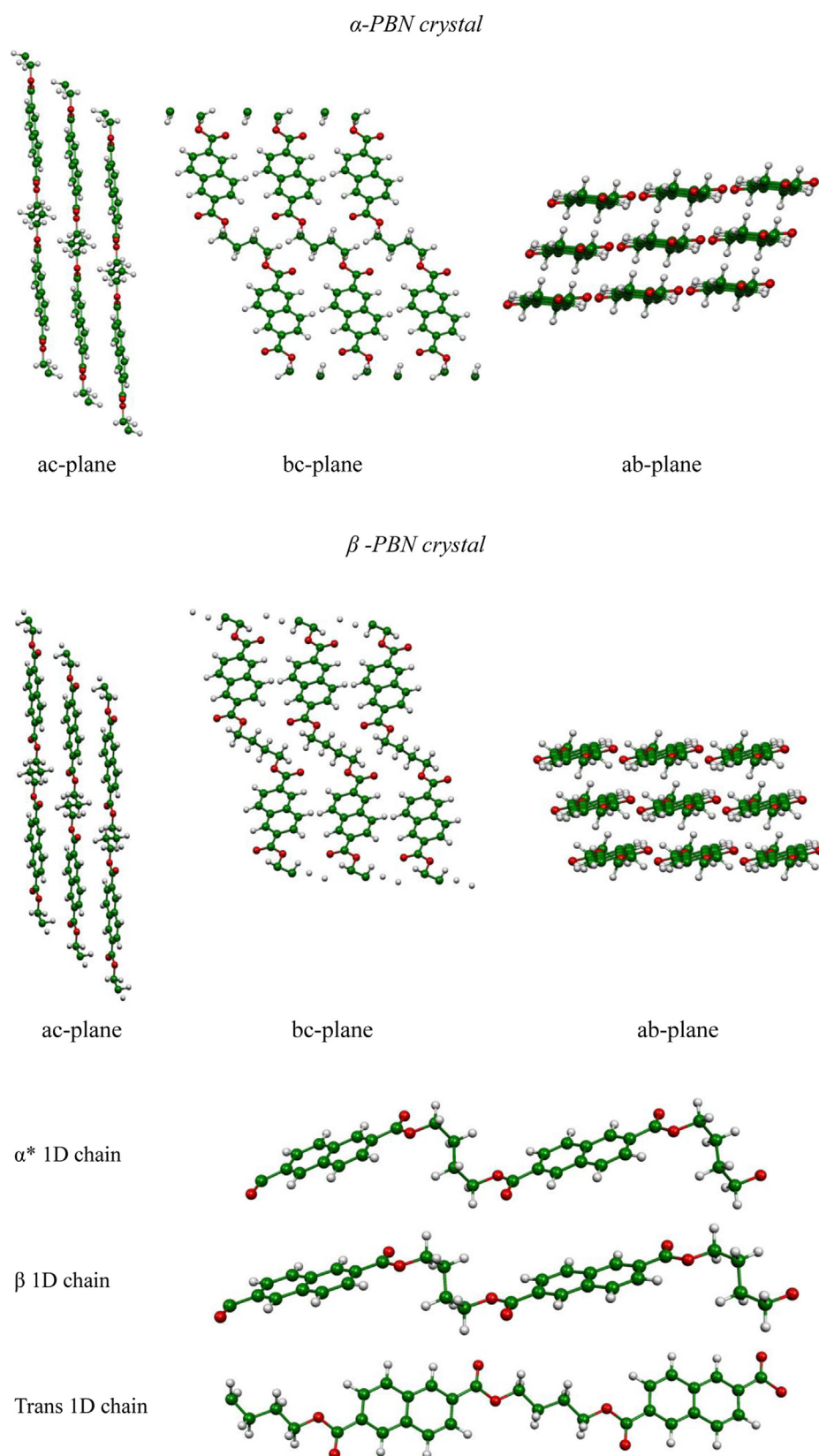
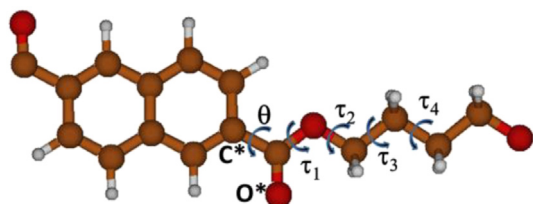


Fig. 1. Sketches of the optimized α and β crystalline structures of PBN and of the 1D model chains possessing α^* , β and trans conformation. In the case of the α chain a GGTG'/G' equilibrium conformation is predicted, contrary to the TGTG'/T calculated for the α crystal and due to these differences this 1D model chain has been labeled as α^* (see text for discussion).

Table 1

Comparison between DFT-D computed (B3LYP-D/6-31G(d,p)) cell parameters and those reported in previous investigations for the α and β phases of PBN. Values of a, b, c parameters are in Å and in degrees for the α, β, γ angles. The values of relevant torsional angles (in degrees), C=O bond distance (in Å) and the C=O stretching frequency (in cm^{-1} , unscaled values) are also reported. A sketch is included for the definition of the torsional angles.

	α -PBN		β -PBN	
	B3LYP-D/ 6-31G(d,p)	expt. (ref. [2])	B3LYP-D/ 6-31G(d,p)	expt. (ref. [2])
a	4.5166	4.87	4.8319	4.55
b	6.6028	6.22	6.1504	6.43
c	14.4705	14.36	14.5529	15.31
α	103.31	100.78	99.19	110.1
β	120.81	126.90	128.62	121.1
γ	105.82	97.93	98.94	100.6



$\tau_1(\text{COC})$	179	177	179	178
$\tau_2(\text{COCC})$	161	123	178	172
$\tau_3(\text{OCCC})$	63	63	66	106
$\tau_4(\text{CCCC})$	180	180	180	180
$\theta(\text{C}^*\text{CCO}^*)$	12	0	4	0
$R_{\text{C=O}}$	1.21827	// ^a	1.22487	1.2292
$\nu_{\text{C=O}}^{\text{Ostr}}$	1777.5	1718	1746.2	1713

^a In the structure of the α form published in Ref. [2] the fractional coordinates of the carbonyl oxygen are not correctly reported. The experimental C=O bond lengths cannot be thus determined.

geometry optimization but an evolution towards a TGTG/T conformation is indeed predicted for both polymorphs, reveals that the polymorphism behavior in PBT and PBN is somewhat different. Our calculations reveal that α - and β -PBN possess a similar TGTG/T conformation on the ester groups and on the methylene sequences of the chain: this finding supports the proposal by Tonelli [13] and Ju et al. [4] who reported indeed that both polymorphs have a similar conformation and differ only in the coplanarity of the ester group with the naphthalene rings, larger in β -PBN. This is indeed predicted by our DFT calculations: the torsional angle $\theta(\text{C}^*\text{CCO}^*)$ has a value of 12° in α -PBN and of 4° in β -PBN, confirming the larger coplanarity observed in the latter. As a result, the electronic charge distribution on the C=O bond is much more delocalized, resulting in longer C=O bonds (1.22487 Å vs. 1.21827 Å) and a softer C=O stretching force constant which results in a smaller C=O stretching frequency. Indeed, the C=O stretching band is experimentally observed at a lower frequency in β -PBN, as also correctly predicted by DFT calculations (1778 and 1746 cm^{-1} in α -PBN and β -PBN respectively) (see next section). In this ground, it should be noticed that in PBT the effects of coplanarity is smaller: indeed our previous calculations [29] reveal that the torsion angle $\theta(\text{C}^*\text{CCO}^*)$ is equal to 6° in α -PBT and 4° in β -PBT (β^*) and also the C=O stretching band shows a smaller frequency shift in the two polymorphs (1758 cm^{-1} and 1745 cm^{-1} in α -PBT and β^* -PBT respectively).

Considering the relative energies of α - and β -PBN, it is found that α -PBN has a lower energy of 1.55 kcal/mol per primitive unit cell (34 atoms), justifying the fact that this polymorph is the most stable form obtained in normal conditions.

In order to further investigate structural effects and related molecular interactions, in Table 2 the DFT computed geometrical parameters of 1D model chains are also reported.

Table 2

Comparison between DFT-D computed (B3LYP-D/6-31G(d,p)) chain repeat distances c' (in Å), torsional angles (in degrees), C=O bond lengths (in Å) and C=O stretching frequencies (in cm^{-1} , unscaled values) of the α^* , β and transplanar 1D model chains (see Computational Details). For the definition of the torsional angles see the sketch reported in Table 1.

	α^* 1D chain	β 1D chain	trans 1D chain
c'	27.6204	28.6766	31.5411
$\tau_1(\text{COC})$	178	180	180
$\tau_2(\text{COCC})$	89	172	180
$\tau_3(\text{OCCC})$	58	64	180
$\tau_4(\text{CCCC})$	180	180	180
$\theta(\text{C}^*\text{CCO}^*)$	1	1	0
$R_{\text{C=O}}$	1.21632	1.21589	1.21597
$\nu_{\text{C=O}}^{\text{Ostr}}$	1798	1798	1797

First, we can verify that in β -PBN the TGTG/T conformation is indeed a minimum of the intramolecular potential since the same conformation is found also for the β 1D model chain, as for PBT. In the case of the α chain, the behavior is completely different: a GGTG/G' is now predicted as a minimum geometry of the isolated chain contrary to the TGTG/T calculated for the crystal. This conformation is the same that has been predicted for PBT, both for the crystal and for the 1D model chain [29]. However, while in PBT this conformation is stable even in the crystal, in PBN GGTG/G' conformation is not stable in the solid state, evolving in the TGTG/T structure described above. This indicates that supramolecular effects related to the packing of the molecules in the crystal are much more important in PBN than in PBT and can destabilize conformations which are energy minima for the isolated chains. Due to these differences between the α -PBN crystal and the respective 1D model chain, the latter one has been labeled as α^* .

It should be also noticed that for all the 1D chains investigated, the ester groups and the naphthalene rings are found to be always coplanar, pointing out that also the conformation on the naphthalene rings is affected by the intermolecular packing interactions, occurring in the crystal.

A quantitative detailed interpretation of these results would require the determination of the torsional barriers in conjunction with intermolecular interaction energies of both PBN and PBT polymorphs: this investigation is out of the aims of the present work and would need an additional computational methodology.

Based on the structural study here reported, we can conclude that our calculations confirm that both α - and β -PBN do possess the same conformation on the ester groups and methylene chains and they differ only for the larger coplanarity of the ester groups and naphthalene rings observed in β . This result supports the interpretation given in Refs. [4,13], even if in the latter a transplanar conformation is proposed for both forms, instead of the TGTG/T conformation that is here predicted. It should be noticed that TGTG/T conformation was predicted also for β -PBT (β^* in Ref. [29]): however, in that case this structure could not explain the pattern observed in the IR spectra, which was due instead to the setting on of an all-trans conformation promoted by mechanical stretching. Therefore, also in the case of PBN, the discussion of the IR spectra is required to unravel completely its polymorphic behavior and to verify if coplanarity effects are indeed enough to explain the differences found experimentally between the two crystals forms.

3.2. IR spectroscopy of PBN polymorphs

In Fig. 2 the experimental spectra of PBN [3,4] and PBT [19] are compared in the most significant frequency ranges to point out the differences between these two polymers.

In the frequency range 1050–850 cm^{-1} , PBT shows peculiar marker bands for the different polymorphs: the 917 cm^{-1} is an

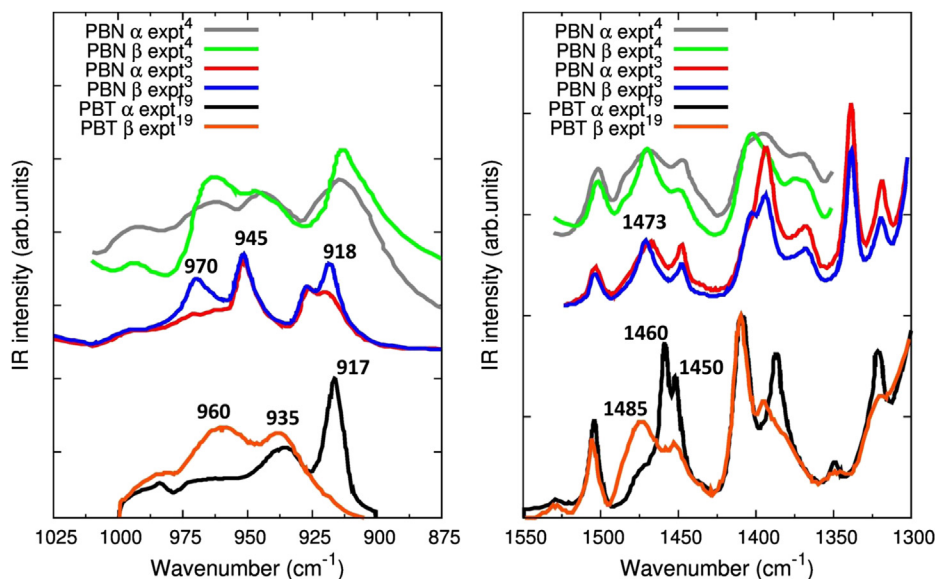


Fig. 2. Comparison of the experimental IR spectra of PBT and PBN polymorphs. For PBT the spectra are taken from Ref. [19] and for PBN from Refs. [3,4].

unambiguous marker of the α form, the 960 cm^{-1} is a marker of the crystal form possessing chains in transplanar conformation, generated by mechanical stretching (β -PBT), while the band at about 935 cm^{-1} is present for both α - and β -PBT. In the case of PBN, a band at 970 cm^{-1} is indeed found for β -PBN and also the band at 945 cm^{-1} is present for both polymorphs. However, at about 920 cm^{-1} both α - and β -PBN show one band; in particular, the band at 918 cm^{-1} (assigned to CH_2 rocking normal modes [3]) shows an increase for higher content of β phase, contrary to the case of PBT where the corresponding feature was a marker of the α form.

In the frequency range $1550\text{--}1300\text{ cm}^{-1}$ other differences can be found: in the case of PBT the bands at $1450\text{--}1460\text{ cm}^{-1}$ and at 1485 cm^{-1} are markers respectively of the α form and transplanar β form, while in PBN no significant differences are found in the same region except for a shift of the band at 1473 cm^{-1} with increasing content of β phase. Furthermore, in PBT the band at 1386 cm^{-1} was assigned to α and the 1393 cm^{-1} to transplanar β form and similarly in PBN the band at 1396 and 1402 cm^{-1} have been assigned respectively to α and β form. The bands in this region have been associated to naphthalene rings vibrations and the observed differences would support some structural differences concerning these groups. Based on Fig. 2, the comparison of the IR spectra of PBT and PBN would indicate that these polymers share both similarities and differences, which need to be clarified.

To this aim, we report in Fig. 3 the comparison between the experimental spectra of PBN polymorphs and the DFT-D spectra obtained for the two crystals and the 1D model chains (transplanar and β conformations). The spectrum of the α^* 1D chain is not reported to avoid confusion, due to its conformation which is different from that predicted for the α crystal, as discussed in the previous section.

We will first analyze the $1800\text{--}1500\text{ cm}^{-1}$ and $900\text{--}600\text{ cm}^{-1}$ frequency ranges: in the former we can observe a clear downshift of the $\text{C}=\text{O}$ stretching band for the β phase due to the increase of the electron conjugation promoted by the larger coplanarity of the ester groups and the naphthalene rings [4]. The DFT-D calculations for the crystals correctly reproduce this shift, in accordance with the smaller $\theta(\text{C}^*\text{CCO}^*)$ predicted for β -PBN. No shifts are predicted for the 1D chain models where coplanarity is found in both cases (see Table 2 and discussion in the previous section).

In the $900\text{--}600\text{ cm}^{-1}$ range a similar pattern is observed for both polymorphs, with the exception of the $840\text{--}820\text{ cm}^{-1}$ region: a component is indeed found at 820 cm^{-1} in Ref. [3] for increasing content of β -PBN and it has been proposed as a marker band for this phase. On the other hand, in the DFT-D computed spectra the opposite trend is found because in this range the lower frequency component at 816 cm^{-1} (scaled value) is found for the α crystal and not for the β one (827 cm^{-1} , scaled value); even 1D model chains cannot explain the experimental spectra. The normal modes associated to these bands (see Supplementary Data) are localized on the naphthalene units (out-of-plane CH deformation mode) and, similarly to the $\text{C}=\text{O}$ stretching frequencies, they can be affected by coplanarity effects, generating the differences found in the spectral pattern. However, we do not have an explanation yet for the disagreement observed between theory and experiments and probably a further experimental analysis should be required to verify the observations reported in Ref. [3] in the $900\text{--}600\text{ cm}^{-1}$ range.

Considering now the other regions of the IR spectrum, the most significant one is the $1050\text{--}850\text{ cm}^{-1}$ range where significant changes are found for the two polymorphs and where the 918 and 970 cm^{-1} bands have been identified as unambiguous markers of the β phase. The spectra computed for the crystals are particularly meaningful here: the comparison between α and β crystals cannot explain the appearance of the 970 cm^{-1} band which cannot be ascribed only to the different coplanarity between the ester groups and the naphthalene rings. Both crystals possess here a low intensity contribution at very similar frequency ($970/972\text{ cm}^{-1}$, scaled values) whose normal mode can be described as CH deformation vibrations localized both on the naphthalene rings and on the methylene chains (see Supplementary Data). Therefore, the appearance of peculiar bands in this region should be related to structures possessing different conformations on the methylene chain. In analogy to the case of PBT, many authors proposed a transplanar structure for β -PBN [3,8,11]: indeed, based on our calculations, we can confirm that a transplanar conformation on the methylene units is responsible for the marker band observed at 970 cm^{-1} , as clearly demonstrated by the comparison of the spectra computed both for the crystals and the β -1D model chain with the spectrum of the transplanar chain. Considering the other marker

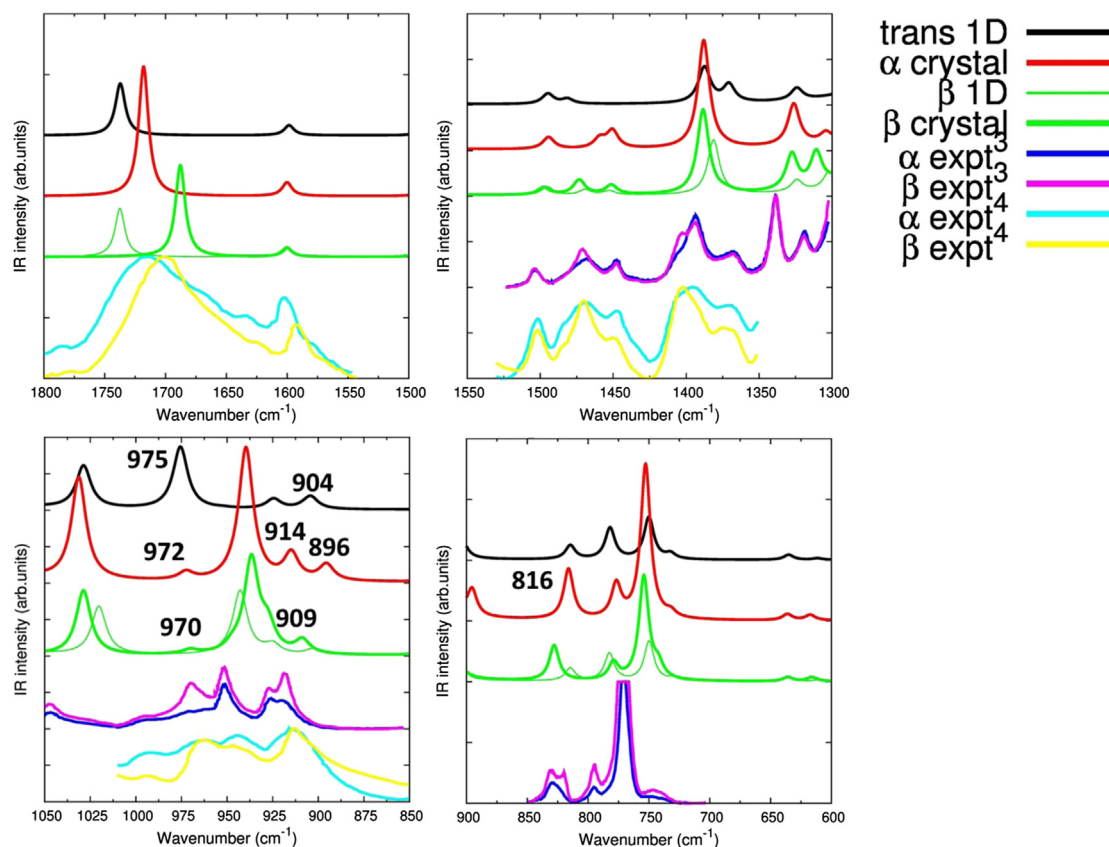


Fig. 3. Comparison of DFT-D computed (B3LYP-D/6-31G(d,p)) IR spectra of the crystals and 1D chain models (β and trans conformations) with the experimental spectra reported in Refs. [3,4] for both polymorphs and the amorphous phase. The computed frequencies are scaled by 0.9665.

band at 918 cm^{-1} , some differences in frequency are found between the α and β crystals (bands at 914 and 909 cm^{-1} respectively, scaled values) which could explain the experimental finding but in any case, the trans 1D chain also shows a band at a similar frequency of the β crystal (904 cm^{-1}) which can be associated to the experimental 918 cm^{-1} band.

Finally, considering the $1550\text{--}1300\text{ cm}^{-1}$ range, we can verify that both the β crystal and the trans chain could explain the higher component at 1470 cm^{-1} ; on the other side, the band at 1402 cm^{-1} could be related again only to the transplanar model if we compare it to the β 1D model.

4. Discussion

The computational investigation of the structural and vibrational properties of PBN polymorphs reveals that this polymer does possess a peculiar behavior that does not parallel the case of PBT.

Starting from the experimental geometries, the full optimization of α - and β -PBT predicted two different crystal structures where different conformations (GGTG'G' vs. TGTG'T) are observed on the methylene chains [29] while the effects due to the coplanarity of the ester groups and the naphthalene rings are less significant. These structures cannot explain the spectra observed after mechanical stretching, which can be interpreted only by taking into account the setting on of a transplanar conformation on the methylene chains.

In the case of PBN, a quite similar conformation is predicted for both α - and β -PBN that can be identified as TGTG'T; on the other side, coplanarity effects are predominant and β -PBN in particular is characterized by a larger coplanarity of the ester groups and the

naphthalene rings. Furthermore, while in PBT both the crystal and the related 1D model chains showed the same conformation, in PBN a different conformation is found for the α crystal and the α (α^*) 1D model chain, thus pointing out that interchain packing effects are more significant in this case. These findings would support the interpretation given by some authors [4,13], reporting that the structural differences between PBN polymorphs should be ascribed to the different coplanarity of the ester groups and the naphthalene rings rather than the different conformation on the methylene chains. This interpretation supports indeed some spectroscopic findings (shift of the C=O stretching band) but, on the other hand, it cannot explain the spectral features appearing in the $1050\text{--}850\text{ cm}^{-1}$ region for the phase generated by stretching or by thermal treatments. Our calculations reveal that also in this case, only a transition to a transplanar conformation can explain the appearance of these peculiar marker bands. This behavior is now in agreement with the interpretation given by other authors [3,8,11] and it is similar to the behavior observed for PBT.

As a result, we can conclude that both the interpretations proposed are acceptable since they describe structural effects which co-exist in PBN. When α -PBN is subjected to a mechanical deformation or isothermal/non-isothermal crystallization at high temperature or under pressure a new polymorph is generated and has been called β -PBN in the previous literature: based on our study we now confirm that this polymorph is characterized both by a transplanar conformation on the methylene chains (different from α -PBN) and by a larger coplanarity of the ester groups and the naphthalene rings than α -PBN.

Both the differences and similarities to the case of PBT are due to the different interplay between intermolecular interactions

(packing of the naphthalene units in the solid state) and intramolecular effects (coplanarity between the ester group and naphthalene ring), generated by π -electron conjugation effects, now more effective in PBN due to the presence of more conjugated naphthalene rings. In these grounds, it should be noticed that the different structural features promoted by the presence of naphthyl rings with respect to phenyl rings have been previously pointed out also in the case poly(ethylene 2,6-naphthalate) (PEN) when compared to poly(ethylene terephthalate) (PET) [7].

5. Conclusions

By means of periodic density functional theory calculations we have investigate PBN polymorphs to give a characterization of the crystal phase transitions observed under mechanical deformation or thermal treatments. Our computational study shows that the PBN polymorphic transitions are characterized either by conformational changes on the methylene chains and on the naphthalene rings, joining the different interpretations reported in previous papers. Our study reveals that PBT and PBN, despite the similarities in their chemical composition, do anyway possess some different structural properties. DFT-D calculations proved to be very accurate in predicting these subtle and delicate effects, shedding light on some aspects that still presented some uncertainties and being again a valuable tool for the characterization of semicrystalline polymers from a molecular point of view. This would be indeed very important in the investigation of structure–property relationship of complex polymeric materials. In this particular case, our work gives a contribution in elucidating the structural properties of PBN polymorphs, paving the way to the investigation of the structural-dependent physicochemical properties of this material.

Appendix A. Supplementary data

References

- [1] Watanabe H. *Kobunshi Ronbunshu* 1976;33:229–37.
- [2] Koyano H, Yamamoto Y, Saito Y, Yamanobe T, Komoto T. *Polymer* 1998;39:4385–91.
- [3] Chiba T, Asai S, Xu W, Sumita M. *J Polym Sci B: Polym Phys* 1999;37:561–74.
- [4] Ju MY, Huang JM, Chang FC. *Polymer* 2002;43:2065–74.
- [5] Ju MY, Chang FC. *Polymer* 2001;42:5037–45.
- [6] Yasuniwa M, Tsubakihara S, Fujioka T, Dan Y. *Polymer* 2005;46:8306–12.
- [7] Tonelli AE. *Polymer* 2002;43:637–42.
- [8] Tashiro K, Cheng J, Ike M. *Macromolecules* 2003;36:359–67.
- [9] Konishi T, Nishida K, Matsuba G, Kanaya T. *Macromolecules* 2008;41:3157–61.
- [10] Cavallo D, Mileva D, Portale G, Zhang L, Balzano L, Alfonso GC, et al. *ACS Macro Lett* 2012;1:1051–5.
- [11] Yamanobe T, Matsuda H, Imai K, Hirata A, Mori S, Komoto T. *Polym J* 1996;28:177–81.
- [12] Yoon KH, Lee SC, Park OO. *Polym J* 1994;26:816–21.
- [13] Tonelli AE. *Polymer* 2002;43:6069–72.
- [14] Yokouchi M, Sakakibara Y, Chatani Y, Tadokoro H, Tanaka T, Yoda K. *Macromolecules* 1976;9:266–73.
- [15] Hall IH, Pass MG. *Polymer* 1976;17:807–16.
- [16] Desborough IJ, Hall IH. *Polymer* 1977;18:825–30.
- [17] Nitzsche SA, Wang YK, Hsu SL. *Macromolecules* 1992;25:2397–400.
- [18] Jakeways R, Smith T, Ward IM, Wilding MA. *J Polym Sci Polym Lett Ed* 1976;14:41–6.
- [19] Stambaugh B, Lando JB, Koenig JL. *J Polym Sci Polym Phys Ed* 1979;17:1063–71.
- [20] Stambaugh BD, Koenig JL, Lando JB. *J Polym Sci Polym Lett Ed* 1977;15:299–303.
- [21] Roebuck J, Jakeways R, Ward IM. *Polymer* 1992;33:227–32.
- [22] Gillette PC, Lando JB, Koenig JL. *Polymer* 1985;26:235–40.
- [23] Dobrovolny-Marand E, Hsu S, Shih C. *Macromolecules* 1987;20:1022–9.
- [24] Kawaguchi A, Murakami S, Fujiwara M, Nishikawa Y. *J Polym Sci Part B Polym Phys* 2000;38:838–45.
- [25] Takahashi Y, Murakami K, Nishikawa S. *J Polym Sci Part B-Polym Phys* 2002;40:765–71.
- [26] Apostolov AA, Fakirov S, Stamm M, Patil RD, Mark JE. *Macromolecules* 2000;33:6856–60.
- [27] Grasso RP, Perry BC, Koenig JL, Lando JB. *Macromolecules* 1989;22:1267–72.
- [28] Gomez MA, Cozine MH, Tonelli AE. *Macromolecules* 1988;21:388–92.
- [29] Milani A, Galimberti D. *Macromolecules* 2014;47:1046–52.
- [30] Galimberti D, Milani A. *J Phys Chem B* 2014;118:1954–61.
- [31] Quarti C, Milani A, Civalleri B, Orlando R, Castiglioni C. *J Phys Chem B* 2012;116:8299–311.
- [32] Galimberti D, Quarti C, Milani A, Brambilla L, Civalleri B, Castiglioni C. *Vib Spectrosc* 2013;66:83–92.
- [33] Quarti C, Milani A, Castiglioni C. *J Phys Chem B* 2013;117:706–18.
- [34] Civalleri B, Zicovich-Wilson CM, Valenzano L, Ugliengo P. *Crystengcomm* 2008;10:405–10.
- [35] Grimme SJ. *Comput Chem* 2004;25:1463–73.
- [36] Grimme SJ. *Comput Chem* 2006;27:1787–99.
- [37] Dovesi R, Orlando R, Civalleri B, Roetti C, Saunders VR, Zicovich-Wilson CM. *Z Krist* 2005;220:571–3.
- [38] Dovesi R, Saunders VR, Roetti C, Orlando R, Zicovich-Wilson cm, Pascale F, et al. *CRYSTAL09 user's manual*. Torino: University of Torino; 2009.
- [39] Torres FJ, Civalleri B, Meyer A, Musto P, Albonia AR, Rizzo P, et al. *J Phys Chem B* 2009;113:5059–71.
- [40] Torres FJ, Civalleri B, Pisani C, Musto P, Albonia AR, Guerra G. *J Phys Chem B* 2007;111:6327–35.
- [41] Ferrari AM, Civalleri B, Dovesi R. *J Comput Chem* 2010;31:1777–84.
- [42] Becke A. *J Chem Phys* 1993;98:5648–52.
- [43] Lee C, Yang W, Parr R. *Phys Rev B* 1988;37:785–9.