Polymorphism of even nylons revisited through periodic quantum chemical calculations

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1. Introduction

Nylons, the commercial name for polyamides, are a family of polymeric materials that are now part of our everyday life [1]. Beyond their common availability, innovative and promising applications are currently under investigation by the scientific community, as in the case of electrospun nanofibers [2–6], nanocomposites [7,8] or applications as biomaterials in nanomedicine.

At the nanoscale, polymorphism is one of the key phenomena ruling the properties of polyamides, being the main actor in the set up of the structure/property correlations that determine a different tensile response, Young modulus or a different thermal response, as for example in the case of Nylon 6 (NY6) where two main α and γ polymorphs co-exist at room temperature. Moreover, depending on the particular class of nylons considered (even, odd, even–even etc.) polymorphism can show a different behavior and peculiar characteristics [1,9]. However, in spite of its importance, the rationalization of the polymorphic phenomena in nylons is a not completely solved issue and it has been investigated also by means of computational approaches, including both classical and quantum chemical simulations [10–14]. The complexity of these phenomena is related to the variety of molecular effects that characterize polyamides and that are related to a subtle balance among different concurrent intermolecular effects (e.g. hydrogen bonding and vdW interactions) and intramolecular effects (e.g. conformational energy, intramolecular non-bonded electrostatic interactions). Since the stabilization of a given polymorph implies peculiar trends of the macroscopic properties a careful understanding of the crystal structure, of its evolution under the external parameters and of the energetics ruling these phenomena is mandatory for a rationalization of the behavior of the material also at the macroscale.

Even, single-numbered nylons NYn here investigated have a $-(NH)-(CH_2)_{n-1}-(C=O)-$ chemical structure (n = 4, 6, 8, 10, 12): NY6 and NY8 crystallize in two different polymorphs, the α and the γ form (sketched in Fig. 1 in the case of NY6), with the former phase that is more stable for NY6 and shorter nylons (NY4) while the latter is more stable for NY8 and longer chains nylons. The two polymorphs are quite different. They possess different space group symmetry and different chain conformation, with the α form showing an all trans conformation and the γ form showing a quasi-extended skew conformation of the CH_2 units adjacent to the amide group.

It has been proposed [1,10–12] that the different crystal packing in the two polymorphs could be related to competitive intermolecular effects: theoretical studies, mainly resorting to classical molecular dynamics simulations [10,11] or quantum chemical simulations carried out on small molecular models [12] have been already reported in the literature, to investigate this behavior; however, a comprehensive investigation on the topic, based on

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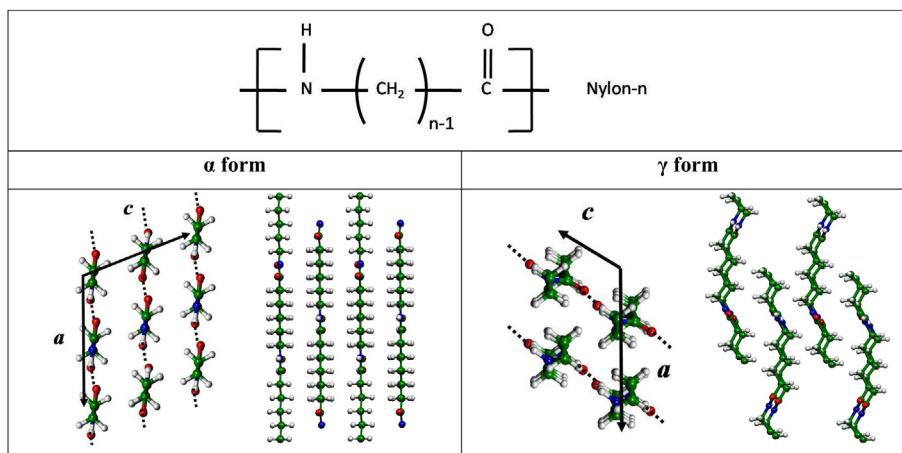
Fig. 1. Structural formula of even nylons-n. Sketches of the crystalline structures of the α and γ polymorphs. Carbon atoms are in green, hydrogen atoms in white, oxigen atoms in red and nitrogen atoms in blue; hydrogen bonds are marked with dots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

accurate, state-of-the-art quantum chemical calculations and on reliable models would be highly coveted.

In very recent years, new computational approaches have been developed and can be applied in polymer science. The CRYSTAL code in particular has been successfully applied to semicrystalline polymers [14–23], revealing very good performances in the reliable prediction of the structural and spectroscopic properties of poly-mer systems belonging to different families, including polyamides [14,18,23]. The main advantages of this code is that it allows accurate Density Functional Theory (DFT) calculations adopting full periodic boundary conditions and hybrid exchange correlation functionals, at a reasonable computational cost. It is then possible to run simulations both on infinite one dimensional (1D) polymer chains but also on the real three dimensional (3D) crystal unit cell, thus joining the possibility to carry out quantum chemical calcu-lations without arbitrary choices of models (i.e. the real crystalline cell is considered), and so avoiding the limitation of previous ap-proaches. Moreover, the possibility to fully take into account the space group symmetry of the system and to adopt reliable correc-tions to the implicit limitation of DFT functional in treating the vdW dispersion interactions are further features of peculiar importance for the simulation of molecular materials.

This computational approach is employed in this paper to study the polymorphism in even single-numbered nylons, ranging from nylon-4 (NY4) to nylon-12 (NY12): for each case, simulations on both the α and γ crystal structures have been carried out to determine the equilibrium geometry and related energetics. Based on a detailed analysis of the different intra- and intermolecular contributions, the molecular phenomena ruling polymorphism in this class of materials will be rationalized.

2. Computational details

Full geometry optimization of the crystal structure and chain conformation of the α and γ polymorphs of nylon-4, -6, -8, -10 and -12 have been carried out by means of the CRYSTAL09 code [24,25] in a fully quantum mechanical framework, using DFT including periodic boundary conditions. Different combinations of DFT functionals and basis sets have been adopted employing both the B3LYP [26,27] and PBE0 [28] hybrid exchange-correlation func-tionals, combined with 6-31G(d,p) and pob-TZVP [29] basis set. Based on previous computational investigations of polyamides [14,18,23], we introduced the empirical correction for dispersion

interaction (DFT-D) proposed by Grimme [30–32] to obtain a more reliable qualitative and quantitative description of van der Waals interactions, which are among the main actors ruling the poly-morphism of nylons and which are not correctly described by standard DFT. The parameters chosen for Grimme corrections are reported in Ref. [14]. In all calculations, the atomic positions and the lattice parameters were fully optimized starting from input struc-tures built on the basis of the experimental geometries of α and γ crystals of nylon-6 from XRD [33–35]. In order to explore confor-mational effects, geometry optimizations have been carried out also on the infinite 1D polymer chains, characterized by the regular conformation shown by the chains in the two crystals (see Fig. 1).

In order to judge about the accuracy of the computations here adopted we report in Table 1 the comparison between DFT computed (B3LYP-D/pob-TZVP) and available experimental cell parameters [33–39] for all the nylons here investigated. As ex-pected a good agreement is found for all the cases, with mean percentage errors which are lower than 3.5% in all the cases, thus supporting the reliability of our computational approach as found also in our previous paper on NY6 polymorphs [14].

However, it should be noticed that, in the case of molecular solids, thermal effects can have a non-negligible role in modulating the cell parameters, as also verified experimentally [40]. Our peri-odic DFT calculations (but also molecular mechanics approaches [10,11]) refer to a 0 K configuration and do not take into account temperature effects (entropic contributions of phonons, molecular geometry fluctuations of angles); therefore the comparison with the result of a complete cell optimization should be taken with care due to the absence of these thermal effects. Due to the good agreement here obtained with the experiments, we believe that thermal effects could be confidently considered small and could explain the minor discrepancies observed; in any case, we do not expected them to affect the trends observed for the different nylons here analysed.

3. Results

3.1. Relative stability of α and γ polymorphs

The relative stability of the α and γ forms of even nylons has been theoretically investigated in few papers [10–12] by using different computational approaches: Dasgupta et al. [10] developed the MSXX force field to run classical simulations specifically for
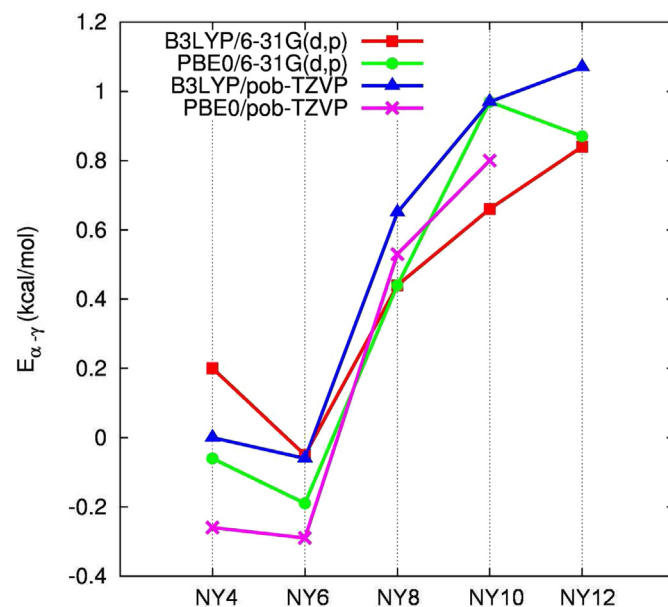
Table 1
Comparison between DFT computed (B3LYP-D/pob-TZVP) cell parameters (values of a,b,c parameters are in Å and in degrees for the β angle) of the α and γ polymorphs od even nylons (NYn, n = 4,6,8,10,12). The percentage error (PE) with respect to the experimental data has been calculated as: PE = (PAR$_{theo}$ − PAR$_{exp}$)*100/PAR$_{exp}$, where PAR means the generic cell parameter (a,b,c). Mean percentage errors (MPE) are also reported by averaging on the PE (absolute value) obtained in each case.

		a	b	c		β
α-NY4	B3LYP-D/pob-TZVP	9.47	12.33	7.37		67.8
	Expt. [36]	9.29	12.24	7.97		65.5
	PE	1.96	0.73	−7.54	MPE 3.41	
γ-NY4	B3LYP-D/pob-TZVP	8.82	11.80	4.79		125.5
	Expt.	//	//	//		//
α-NY6	B3LYP-D/pob-TZVP	9.50	17.43	7.42		68.0
	Expt. [33,34]	9.56	17.24	8.01		67.5
	PE	−0.68	1.07	−7.41	MPE 3.05	
γ-NY6	B3LYP-D/pob-TZVP	8.84	16.94	4.78		126.3
	Expt. [35]	9.33	16.88	4.78		121.0
	PE	−5.26	0.33	0.06	MPE 1.88	
α-NY8	B3LYP-D/pob-TZVP	9.52	22.53	7.47		67.6
	Expt. [37]	9.64	22.4	8.03		65
	PE	−1.27	0.58	−6.98	MPE 2.94	
γ-NY8	B3LYP-D/pob-TZVP	8.85	22.05	4.77		126.6
	Expt. [38]	9.54	21.9	4.77		120
	PE	−7.25	0.71	0.08	MPE 2.68	
α-NY10	B3LYP-D/pob-TZVP	9.53	27.63	7.50		67.2
	Expt.	//	//	//		//
γ-NY10	B3LYP-D/pob-TZVP	8.85	27.17	4.77		126.8
	Expt. [38]	9.56	26.9	4.78		120
	PE	−7.39	0.99	−0.30	MPE 2.89	
α-NY12	B3LYP-D/pob-TZVP	9.56	32.73	7.51		66.7
	Expt.	//	//	//		//
γ-NY12	B3LYP-D/pob-TZVP	8.86	32.28	4.76		126.9
	Expt. [39]	9.58	31.9	4.79		120
	PE	−7.54	1.18	−0.68	MPE 3.13	

progressively increases the contribution due to their efficient intermolecular packing, which becomes predominant starting from nylon-8, thus stabilizing the γ form. Despite the general agreement between the different computational approaches, there are intrinsically some limitations which could prevent a more detailed investigation of the molecular effects ruling nylon polymorphism. On one hand, classical force field approaches bring the implicit arbitrariness related to the choice of empirical potential energy functions and parameters which could not be able to consider properly all the peculiar interactions taking place (such as non standard intramolecular coulomb interactions [41]). Moreover, some discrepancies in the relative stabilities of nylons with very large aliphatic segments have been also observed when carrying out monte carlo simulations with respect to force-field based energy calculations [1]. On the other hand, quantum chemical calculations on small molecular models bring an arbitrariness in the choice of reliable molecular models which could influence the quantitative results or could not describe completely the real interactions having place in a macromolecular crystal. As an example, a dependence of the relative stability of α and γ conformations on the number of residues adopted to generate the oligomer model of an infinite polymer chain have been observed [41]. Our approach, that resorts on a quantum mechanical treatment carried out on the complete crystalline cell, allows to avoid most of these limitations. In Fig. 2, the energy difference between the α and γ polymorphs (E$_{α-γ}$=E$_α$−E$_γ$) is reported from NY4 to NY12, as obtained by the geometry optimization of the 3D unit cell of the two forms for different combinations of DFT functional/basis set. Related numerical values are reported in Table 2.

Fig. 2 reveals that for most of the functional/basis set combinations, the α form is predicted as the most stable one in the case of nylon-4 and nylon-6, in agreement with experimental investigations [1]. Only for B3LYP-D/6-31G(d,p), the γ form turns out to be the preferred one in NY4, contrary to previous theoretical

nylon polymers while Aleman and Casanovas [11] adopted both monte carlo simulations and energy calculations by using again a force field approach to investigate the structural properties of very large nylons. In addition to these classical approaches, a pioneering quantum chemical investigation has been presented by Bernadò et al. [12] where the stability of these polymorphs has been evaluated by reconstructing the energy of the whole crystal as the sum of group contributions due to the intermolecular and intramolecular interactions occurring in and between small molecular fragments. Moreover, the same research group carried out further quantum chemical investigations to characterize the peculiar conformational and intramolecular interactions having place in nylon polymers, adopting also in these cases small molecular models (oligomers) of the whole polymer chains [41]. The general results of these studies, confirming the previous interpretations [1], is that the α form is the stable one for nylon-4 and -6 while the γ form is predominant in the even nylons from NY8 up. This behavior has been explained based on the balance between competing intermolecular effects: indeed, in the α form the hydrogen bonds are more efficient than in γ form, at the expense of a non optimum packing of the CH$_2$ groups; at the opposite, in the γ form the optimum packing of the methylene units dominate over hydrogen bonding. Therefore, in polymers with shorter monomeric units such as NY4 and NY6, hydrogen bonding interactions are predominant and stabilize the α form preferentially. For nylons with larger monomeric units, the increasing number of CH$_2$ units

Fig. 2. Relative energies (for single monomer units) of the α and γ polymorphs (E$_{α-γ}$ = E$_α$ − E$_γ$) of even, single numbered nylons ranging from NY4 to NY12. Units of kcal/mol. E$_α$, E$_γ$ are the DFT computed total energy of the two 3D crystals respectively. The results obtained by using two DFT functionals (PBE0 and B3LYP, with Grimme corrections) and two basis sets (6-31G(d,p) and pob-TZVP) are reported. In the case of PBE0-D/pob-TZVP calculation on NY12, no convergence in the geometry optimization has been obtained and thus no results are indicated. Numerical data are reported in Table 2.

Table 2

Values of the relative energies between α and γ crystals ($E_{\alpha-\gamma} = E_\alpha - E_\gamma$) per single monomer unit, as obtained for different DFT functionals and basis sets. Units of kcal/mol. In the case of PBE0-D/pob-TZVP calculation on NY12, no convergence in the geometry optimization has been obtained and thus no results are indicated.

3D crystal	B3LYP-D/6-31G(d,p)	PBE0-D/6-31G(d,p)	B3LYP-D/pob-TZVP	PBE0-D/pob-TZVP
NY4	0.20	−0.06	−0.01	−0.26
NY6	−0.05	−0.19	−0,06	−0.29
NY8	0.44	0.44	0.65	0.53
NY10	0.66	0.97	0.97	0.80
NY12	0.84	0.87	1,07	//

studies and structural determinations. It should be noticed, however, that, when investigating supramolecular interaction, computational effects such as basis set superposition error (BSSE) [42], can influence significantly the energetic description of intermolecular interactions. This is the reason why simulations have been also carried out with the more extended (and less BSSE sensitive) pob-TZVP basis set which should give more accurate quantitative values of the relative energies. The stabilization of the α form in NY4 and NY6 found in the other calculations is in agreement with previous investigations [10]: in the case of NY6, the relative energy $E_{\alpha-\gamma}$ ranges from −0.05 to −0.29 kcal/mol per monomer chain in agreement with the −0.323 kcal/mol [10] and −0.50 kcal/mol [12] values previously suggested. With the exception of B3LYP-D/6-31G(d,p) in the case of NY4 the relative energy $E_{\alpha-\gamma}$ ranges from −0.01 to −0.26 kcal/mol and in all the cases it is smaller in magnitude than for NY6. This result is again in agreement with previous molecular mechanics calculations on nylon polymers [10] where a relative $E_{\alpha-\gamma}$ energy of −0.272 kcal/mol is found for NY4 with respect to the −0.323 kcal/mol value found for NY6. Considering nylons with increasing number of CH_2 units, the γ form becomes the most stable one already for NY8 ($E_{\alpha-\gamma}$ ranging from 0.44 to 0.65 kcal/mol) and its stability increases for NY10 ($E_{\alpha-\gamma}$ ranging from 0.66 to 0.97 kcal/mol) and NY12 ($E_{\alpha-\gamma}$ ranging from 0.84 to 1.07 kcal/mol). These trends are in agreement both with the experimental evidences and with previous investigation [10−12]: in Ref. [12] in particular, the results of quantum chemical calculations on small model systems predicted an $E_{\alpha-\gamma}$ energy of 0.63 and 0.82 kcal/mol respectively for NY8 and NY10, showing a very similar trend to the one here presented (0.53 and 0.80 kcal/mol is found at the PBE0-D/pov-TZPV level). It should be noticed that in the case of NY12 while B3LYP-D calculations always predict a larger $E_{\alpha-\gamma}$ energy with respect to NY10, a lower value (0.87 vs 0.97 kcal/mol) is found for PBE0-D/6-31G(d,p) calculation. In Ref. [11], based on monte carlo simulations, a decreasing trend in $E_{\alpha-\gamma}$ has been predicted starting from NY12, suggesting that the preferential stability of the γ form would decrease for nylon possessing a very large number of CH_2 units in the chain. Unfortunately, we could not reach in any way convergence in the geometry optimization of NY12 at PBE0-D/pob-TZVP level and thus we cannot check if our results are due to some computational effects, as the afore-mentioned BSSE, or if they are describing some physicochemical effects which are best described by PBE0 functional with respect to B3LYP.

Aside from these details, our computational study confirms that the α form is the preferred one for nylon-4 and -6, while γ form results to be more stable starting from nylon-8. In previous investigations, this behavior has been interpreted mainly in the light of intermolecular effects, and in particular as due to the balance between hydrogen bonding effects (more efficient in the α form) and optimum packing of CH_2 units (more efficient in the γ form). On the other hand, the present authors have already pointed out the role of the conformation potential of the isolated chain on the polymorphism of NY6 [14]. In the following sections, both the intramolecular interactions ruling the conformational behavior and

intermolecular interactions due to hydrogen bonding and packing of CH_2 chains will be analyzed in detail.

3.2. Conformational effects

An intramolecular/conformational investigation has been carried out by means of geometry optimization and energy evaluation of infinite 1D chains possessing respectively the transplanar conformation, typical of the α polymorph, and the skew conformation of the CH_2 units adjacent to the amide group, typical of the γ polymorph (see Fig. 1). The relative energies are plotted in Fig. 3 and related numerical values are reported in Table 3. As a first result, we found that the typical conformations observed in the two crystals (i.e. a fully extended structure for the α form and the quasi-extended structure for γ form) are maintained after the optimization carried out on the isolated infinite chain, that is in absence of any intermolecular interactions. In other words, these two conformations correspond to real minima of the torsional potential of the chain and they are not ruled by the packing effects taking place in the crystal.

Considering the relative energy of the two conformations as reported in Fig. 3 and Table 3, it is interesting to notice that the quasi-extended γ conformation is the most stable one for all the considered nylons, independently of the computational method employed: when adopting the more extended pob-TZVP basis set the relative energy is found to be about one half of that obtained by
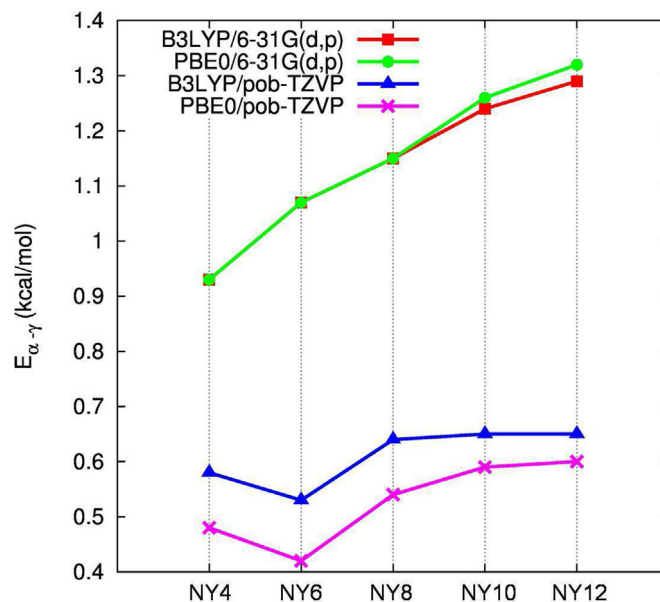
Fig. 3. Plot of the relative energies per single monomer unit $E_{\alpha-\gamma}^{1D} = E_\alpha^{1D} - E_\gamma^{1D}$ with $E_\alpha^{1D}, E_\gamma^{1D}$ being the DFT computed total energy of the two 1D infinite chains possessing respectively α and γ conformation. Units of kcal/mol. The results obtained by using two DFT functionals (PBE0 and B3LYP, with Grimme corrections) and two basis sets (6-31G(d,p) and pob-TZVP) are reported. Numerical data are reported in Table 3.

Table 3
Values of the relative energies per single monomer unit between 1D infinite chains possessing α and γ conformation ($E_{\alpha-\gamma}^{1D} = E_{\alpha}^{1D} - E_{\gamma}^{1D}$), as obtained for different DFT functionals and basis sets. Units of kcal/mol.

1D chain	B3LYP-D/6-31G(d,p)	B3LYP-D/pob-TZVP	PBE0-D/6-31G(d,p)	PBE0-D/pob-TZVP
NY4	0.93	0.58	0.93	0.48
NY6	1.07	0.53	1.07	0.42
NY8	1.15	0.64	1.15	0.54
NY10	1.24	0.65	1.26	0.59
NY12	1.29	0.65	1.32	0.60

6-31G(d,p) basis set but in any case γ conformation is the preferred one. Moreover, its stability is found to slightly increase with the number of CH_2 units in the chain, already giving a possible explanation of the fact that, starting from NY8, the γ polymorph becomes the most stable one and its stability grows when considering NY10 and NY12. Interestingly, for NY6, the stability of the γ conformation is slightly lower than in NY4 and this behavior can be one of the factors explaining why the α polymorph in NY6 is more stable than in NY4.

The most important result of this analysis is that peculiar intermolecular effects play a significant role in the case of NY4 and NY6: supramolecular packing interactions tend to stabilize the α structure in these two polymers, despite the preference of their single chains to adopt the quasi-extended γ conformation. On the other hand, for the other nylons with $n > 6$, intramolecular interactions cooperate with the intermolecular ones in stabilizing the γ form.

From the computational perspective, it is interesting to compare the results obtained here for infinite 1D chains with regular conformations with the results presented in a previous work [41] where conformational effects in nylons have been investigated by using finite length molecular models of the polymeric chains. In that work indeed, while the γ conformation has been found to be always the preferred one for nylons NYn with $n > 6$; the α conformation was found to be the most stable for $n \leq 6$, depending on the number of residue adopted in the molecular models. This demonstrate that the arbitrariness in the choice of the finite-length molecular model adopted (not required in our approach) could influence significantly the final results and interpretations.

3.3. Analysis of intermolecular packing interactions

The next step in the understanding of the polymorphic behavior of even nylons requires a detailed investigation of intermolecular interactions.

A net evaluation of these interactions can be carried out by calculating the cohesive energy of each crystal as the difference between the energy of the 3D crystal and the energy of the isolated 1D chain, both normalized on one monomeric unit. The trends so obtained are reported in Fig. 4 and associated numerical data in Table 4 referred to B3LYP-D/pob-TZVP calculations. In the following discussion we will adopt this computational method in order to obtain numerical values as accurate as possible and to carry out stable calculations for all the systems investigated.

Cohesive energies show a very clear and peculiar behavior: given the larger dimension of the monomeric units and the increasing number of interacting CH_2 units, these energies obviously linearly decrease moving from NY4 to NY12. However, the slope of the two lines associated respectively to α and γ polymorphs is different and it is larger in particular for the latter. Indeed, the cohesive energy is larger for the α form in the case of NY4, they are almost equal for NY6 and NY8 in particular and then it becomes larger for the γ form in NY10 and NY12. For NY8 in particular, the two energies are practically the same, thus

indicating that NY8 is the turning point where a transition in the relative stability of α and γ crystals could take place due to intermolecular effects, stronger in the α form for NY4 and NY6 and in γ form for NY10 and NY12.

In order to give a deeper interpretation of the trend observed and thus of the relative stabilities of α and γ polymorphs (where both intra- and intermolecular effects co-exist), we have to go further in the detailed investigation of supramolecular effects, explicitly considering the different contributions (hydrogen bonding vs close packing of CH_2 groups) taking place.

It is well-known that commonly-used exchange-correlation functionals (such as B3LYP) lack the description of van der Waals (vdW) dispersion interactions, that are an essential ingredient in all molecular materials and of special importance in our present cases. For this reason, the correction proposed by Grimme (based on a semiempirical approach) [30–32] has been adopted in our calculations, as explained in the computational details. According to this approach, a two-body potential energy contribution of the type ($-C_6/R^6$) is added to the total DFT energy to recover the correct description of vdW interactions. This correction further allows to estimate the contribution due to the intermolecular vdW interactions between CH_2 units. We indeed carried out two types of new calculations: in the first one no Grimme corrections are introduced on all the atoms while in the other one they are
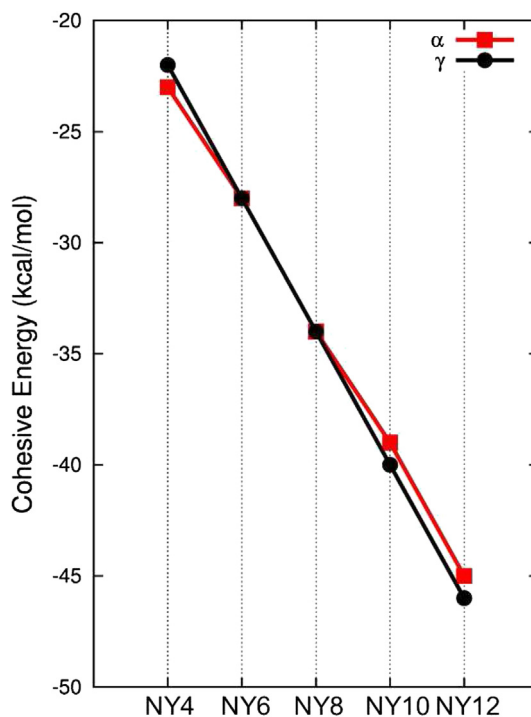
Fig. 4. DFT computed (B3LYP-D/pob-TZVP) cohesive energies $E_{coh} = E^{3D} - E^{1D}$ (kcal/mol per single monomer unit) with E^{3D}, E^{1D} being the total energy of the crystal and of the infinite isolated chain.

Table 4

Values of cohesive energies per single monomer unit, Grimme intermolecular vdW energy contribution of CH_2 units, Grimme intermolecular vdW energy contribution of CH_2 units normalized on a single CH_2 group, and H-bonding energy contribution. Units of kcal/mol The definition of the different terms is reported in the text. These data have been obtained by means of B3LYP-D/pob-TZVP calculations. Units in kcal/mol residue.

	Cohesive energy	Grimme intermolecular Vdw contribution all CH_2	Grimme intermolecular Vdw contribution per CH_2	H-bonding contribution
α-NY4	−23.02	−5.66	−1.89	−17.37
γ-NY4	−22.44	−5.96	−1.99	−16.48
α-NY6	−28.90	−10.93	−2.19	−17.97
γ-NY6	−28.30	−11.69	−2.34	−16.61
α-NY8	−34.17	−16.62	−2.37	−17.54
γ-NY8	−34.18	−17.60	−2.51	−16.58
α-NY10	−39.80	−22.57	−2.51	−17.23
γ-NY10	−40.12	−23.54	−2.62	−16.58
α-NY12	−45.65	−28.62	−2.60	−17.03
γ-NY12	−46.07	−29.51	−2.68	−16.56

introduced only on CH_2 groups. The differences in the total energies of these simulations give an estimation in each case of the total (intermolecular + intramolecular) vdW interaction energies between CH_2 units belonging to the different adjacent polymer chains. In order to obtain the intermolecular contributions only, intramolecular vdW interactions have to be removed. These terms can be evaluated by using a similar procedure: indeed their values can be evaluated for each case by carrying out two single point calculations for the infinite isolated polymer chains where Grimme's correction is either added on CH_2 groups only or it is completely missing. The energy difference between the latter and the former gives the intramolecular vdW contributions between CH_2 groups which should be subtracted from the total vdW energies to isolate only the intermolecular terms, reported in Table 4. The results obtained immediately give a clear description: in all the cases the contribution due to the packing of CH_2 groups is slightly larger (more negative) in the case of the γ form, thus supporting the fact that in this crystal a better arrangement between CH_2 units is obtained. It is also interesting to verify that, for increasing number of CH_2 units, this vdW contribution, normalized per each single CH_2 group, increases with the length of the methylenic part of the chains. In other words, the bigger is the number of CH_2 in the chain, the more efficient is their packing, both in the case of α and γ crystals. This is probably due to the larger freedom of CH_2 groups in monomeric units of larger length.

Having now demonstrated that vdW interactions between CH_2 groups are more efficient for the γ form, it is necessary to get information about the energetic of the hydrogen bonding in each case.

The cohesive energy E_{coh}, can be considered the sum of different intermolecular interactions:

$$E_{coh} = E^{DFT}_{H-bond} + E^{grimme}_{CONH} + E^{grimme}_{CH_2-CONH} + E^{DFT}_{VdW} + E^{grimme}_{CH_2}$$

(1)

where E^{DFT}_{H-bond} is due to the DFT contribution of the hydrogen-bonding, E^{grimme}_{CONH} is the Grimme vdW contribution of the amide groups (that is the dispersion interaction term in hydrogen-bonding not taken into account by DFT), $E^{grimme}_{CH_2-CONH}$ is the Grimme vdW contribution of the amide groups interacting with CH_2 groups of the adjacent chains, E^{grimme}_{CH2} is the Grimme intermolecular vdW contribution of CH_2 units analyzed previously and E^{DFT}_{VdW} is the DFT contribution due to VdW interactions.

The global energy associated to the hydrogen bonding (E_{H-bond}) between neighboring chains has been calculated subtracting from this cohesive energy the Grimme vdW contribution of CH_2 units:

$$E_{H-bond} = E_{coh} - E^{grimme}_{CH_2} = E^{DFT}_{H-bond} + E^{grimme}_{CONH}$$
$$+ E^{grimme}_{CH_2-CONH} + E^{DFT}_{VdW} \sim E^{DFT}_{H-bond}$$
$$+ E^{grimme}_{CONH}$$

We already commented that DFT alone cannot take into account properly vdW interactions and thus we can straightforwardly assume the last term E^{DFT}_{VdW} as negligible. Moreover, due to the large distance, also the Grimme vdW contribution between CH_2 groups and the amide groups $E^{grimme}_{CH_2-CONH}$ is of secondary importance. The difference so calculated ($E_{coh} - E^{grimme}_{CH_2}$) can be thus related mainly to the contribution of hydrogen bonding ($E^{DFT}_{H-bond} + E^{grimme}_{CONH}$) and it is reported in the last column of Table 4. Also in this case a very clear trend is obtained: in all the cases the H-bonding contribution is larger for the α form, indicating that in this polymorph the structure maximizes this interaction while CH_2 groups are less efficiently packed.

A last indication on the intermolecular interactions taking place in the two different polymorphs and of their relative importance can be obtained by evaluating the energy difference between the vdW CH_2 and H-bonding contribution in the α and γ forms (Table 5). These differences, together with the energy contribution of intramolecular (conformational) interactions, will be important to predict the relative stability of α and γ polymorph.

It is evident from the energy differences, reported in Table 5, that the CH_2 interactions, dominant in the γ form (positive energy difference), become more for this polymorph for greater number of CH_2 units, thus increasing the tendency to assume a γ structure. On the other hand, the H-bonding stabilization, dominant in the α form (negative energy difference) lowers from NY6 to NY12, therefore decreasing the tendency of the polymer to assume the α structure. Both these trends suggest again an evolution towards the γ structure for increasing number of CH_2 units and it will be the balance

Table 5

Energy differences per single monomer unit between α and γ crystals of the total Grimme vdW energy contribution of CH_2 units and H-bonding energy contribution reported in Table 4 (column 3 and 5). Units of kcal/mol residue. Data obtained at the B3LYP-D/pob-TZVP level of theory.

	$\Delta E\alpha$-γ CH_2 contribution	$\Delta E\alpha$-γ H-bonding contribution
NY4	0.30	−0.88
NY6	0.76	−1.36
NY8	0.97	−0.96
NY10	0.97	−0.65
NY12	0.88	−0.47

among these intermolecular terms and the intramolecular energy that will determine the most stable crystal structure observed for even nylons, as discussed in the next section.

4. Discussions

As a final analysis it is now interesting to compare the intermolecular energies reported in Table 5 with the conformational energies reported in Table 3 in order to give a final interpretation of the relative stability of even nylons polymorphs based on the interplay between intra- and supramolecular interactions. Starting from NY4, it can be seen indeed that hydrogen bonding tends to stabilize the α form since it gives a dominant contribution of about 0.6 kcal/mol with respect to CH_2 packing interactions that would stabilize the γ form. However, the γ conformation (i.e. the intramolecular contribution) is found to be more stable of practically the same amount of energy (see Table 3), thus balancing net intermolecular effects: this explains why, according to B3LYP-D/pob-TZVP simulations, these two polymorphs are predicted to be almost isoenergetic. For NY6, the intermolecular effects would still promote the occurrence of the α polymorph by, again, a contribution of 0.6 kcal/mol. In this case however, the intramolecular contribution is slightly less than in NY4, thus showing that the stabilization energy associated to the γ conformation of the chain is not able to overcome the intermolecular stabilization resulting by packing in the α structure. Moving now to NY8, we can verify that the H-bonding and CH_2 packing contribution are practically the same and balance one another; therefore the tendency of this polymer to adopt a γ structure is mainly promoted by the larger stability of the γ conformation. NY8 is the turning point in the polymorphic behavior of nylons: indeed considering now NY10 and NY12 the larger intermolecular contribution due to CH_2 packing interactions tend to promote a γ structure concurrently with conformational effects.

5. Conclusions

Thanks to state-of-the-art DFT calculations we revisited the polymorphic behavior of even nylons to shed light on the associated intra and intermolecular phenomena. In NY4 and NY6 hydrogen bonding interactions, that promote the occurrence of the α structure, dominate over CH_2 packing interactions and conformational effects both more favorable to the γ structure. On the other hand, in NY10 and NY12 CH_2 packing interactions dominates and the joint contribution of intramolecular effects explains why a γ structure if found for these materials. In NY8, instead, intermolecular contributions balance by packing of the alkyl chains and hydrogen bonds and the setting on of the γ structure is ruled by conformational effects only.

Beyond clarifying the role of subtle molecular phenomena in modulating the structural properties of nylons polymers, the present study shows the importance of molecular modeling in the understanding of structure-properties correlations in polymer materials, providing information which is of fundamental importance for their characterization and hardly accessible from experiments.

Even if the infinite crystal does not take into account the existence of finite dimension effects (e.g. the lamellar morphology of polymers, chain folds ecc) which could influence the relative stability of polymorphs, in any case it is an unavoidable starting point for the modeling of crystalline polymers.

The additional possibility to compute the spectroscopic response [14–23], paves the way to the application of quantum chemical calculations in different branches of polymer science and technology. Furthermore, it should be noticed that the current accuracy of these methods paves the way to use molecular modeling as a design tool, to predict the response of the material prior to wider and expensive experimental investigations.

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