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ORIGINAL CONTRIBUTION

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Computer experiments on crystalline nylons: structural analysis of nylons with large aliphatic segments

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Abstract A theoretical study based on force-field calculations has been performed to investigate the structural preferences of crystalline even nylons *n* with large and very large aliphatic segments. Atomistic energy calculations and Monte Carlo simulations were carried out considering the conventional α and γ forms of nylons 10, 12, 18, 24, and 32. Results indicated that the γ form is the most favored for nylons 10, 12, 18, and 24. However, the γ structure was unstable for nylon 32, a polymer in which the density of hydrogen bonds is almost negligible. In this case, the α arrangement is energetically more favored than the γ one.

Keywords Nylon · Monte Carlo simulations · Crystalline structure · Force-field calculations · Aliphatic segment

Introduction

The two most common crystalline structures found in nylons *n* are those named the α and γ forms [1, 2]. The α form was originally proposed by Holmes et al. for nylon 6 [1]. It consists of hydrogen-bonded sheets made of antiparallel chains in a fully extended conformation, which are progressively shifted 1.53 Å along the *a*-axis. These sheets pack in a monoclinic lattice shearing in a recuperative manner along the *c*-axis, a displacement of $\Delta c = 3c/14$ units (3 averaged main chain bonds) being originally proposed. It should be noted that the shifting distance along the *a*-axis is evidenced by X-ray diffraction data, whereas the shearing along the *c*-axis cannot be established from experimental data. Atomistic modeling tools have been used to reinvestigate this aspect of the α form of nylon 6. León et al. [3] proposed a statistical model constituted by a mixture of Δc values ranging from $2c/14$ to $6c/14$ units (the lowest energy arrangement was attributed to a shearing of $\Delta c = 4c/14$ units), while Li et al. [4] supported the model of Holmes et al. [1].

Arimoto et al. described the γ form of nylon 6 in the middle of the sixties [2]. In this structure the chains adopt a quasi-extended conformation similar to the pleated sheet of proteins, which is produced by the *skew* arrangement of the methylene groups next to the amide. Two distinctive features are associated with this characteristic conformation: (a) the repeat unit length is shortened by about 0.35 Å per amide group; and (b) the amide groups are tilted (~60°) towards the plane defined by the aliphatic segment of the chain. Accordingly, hydrogen bonds are established between chains of different sheets favoring pseudohexagonal packing. In this structure the sheet displacement is restricted near to zero, since the arrangement with the amide groups placed at nearly the same height is the only one able to form the hydrogen bonds. Bermúdez et al. [5] carefully analyzed this point for odd–odd nylons *n*,*n* + *2*.

The α form is largely predominant in the even nylons 4 and 6, the odd nylons, and the even–even nylons *n*,*m*, while the γ form predominates in the even nylons from 8 upwards and in even–odd, odd–even, and odd–odd

nylons *n*,*m* [6]. It should be noted that for even nylons *n* the relative stability between the two forms reverses above nylon 6. This is because the packing of the aliphatic segments is more favorable in the γ form than in the α form, the stability of the former increasing with the number of CH_2 units. It should be also emphasized that the relative stability between the α and γ forms is of great importance, since mechanical properties are dramatically influenced by the crystal structure. Thus, Young's moduli of the α form are larger than for the γ form. Similarly, the crystal packing affects the elastic stiffness constants.

Although nylons with industrial importance adopt the conventional α and γ forms, the number of computational studies comparing the stability of these two structures in even nylons *n* is rather scarce. Dasgupta et al. [7] used the MSXX force field, which was derived from ab initio quantum mechanical calculations, to predict that the α form is favored with respect to the γ form for nylons 4 and 6. The same authors found that nylon 8 prefers the γ form rather than the α one. More recently, Bernadó et al. [8] used a model based on group contributions, which was also derived from ab initio quantum mechanical calculations, to investigate the relative stability between the two forms for nylons 6, 8, and 10. It was found that the α form is favored for nylon 6, while the γ form is stabilized for nylons 8 and 10. The energy differences predicted in these studies were quite small, indicating that the two crystalline forms can be detected for such polymers. Indeed, for nylon 6 the γ phase can be transformed to the α phase by various treatments, including pressure. On the other hand, the α form has been observed for nylons 8 and 10, even though the γ is the predominant form.

Experimental studies have revealed that nylon 12 is the highest member of even nylons *n* for which the α form has been observed [9], the γ being the unique form observed for nylons 16 and 18 [10, 11]. In spite of this limitation, a comparative energy analysis of the α and γ structures for even nylons *n* with $n > 12$ is desirable to evaluate the influence that the long aliphatic segments may exert on the molecular arrangement.

Driven by the improving methodology and the increasing power of computers, molecular simulation techniques have progressed very rapidly in recent years. Indeed, atomistic modeling by means of molecular dynamics or Monte Carlo (MC) simulations is currently considered a powerful tool for studying the structure and properties of both crystalline and amorphous polymers. In this work we use computer simulation methods to investigate the relative stability between the α and γ forms in even nylons *n* with large and very large aliphatic segments, i.e., *n* ranging from 10 to 32. It is worth noting that computer experiments of crystalline systems exhibit two important advantages: (i) well-defined and purely crystalline systems can be studied; and (ii) unobserved crystalline structures can be generated, analyzed, and compared with the observed ones. Thus, simulation tools do not cope with synthetic difficulties, semicrystallinity, or incomplete orientation of the crystallites.

Methods

Molecular models

Calculations were performed considering all atoms explicitly, including the hydrogen atoms of the CH_2 groups. Standard values were used for the bond lengths and bond angles, which were taken from the Amber libraries [12] as well as from previous ab initio calculations on nylon *n* chains [13].

Two models were considered for the α form of even nylons *n*. They can be described as a crystal lattice in which hydrogen bonds are aligned perpendicular to the chain axis and consecutive sheets are shifted along the *c*-axis by 3 (Holmes model) [1] or 4 (León model) [3] averaged main chain bonds. Both models were fitted to the monoclinic cell reported for nylon 6: $a = 9.56$ Å, $b = 8.02$ Å, and $\gamma = 67.5°$ [1,3]. The α form is depicted in Fig. 1 for nylon 12.

The cell parameters experimentally determined for nylon 10 were used for the γ form of even nylons *n*: $a = 4.78$ Å, $b = 9.56$ Å, and $\gamma = 120.0°$ [7]. However, it should be mentioned that very similar parameters were reported for nylon 12 [14, 15]. The more characteristic trends of the γ form are pseudohexagonal packing, i.e., chains are separated by 4.78 Å along both the *a*- and *b*-axes, and the formation of hydrogen bonds between chains of different sheets. These features are illustrated for nylon 12 in Fig. 2.

Force-field calculations

Energy calculations and MC simulations were performed with the PCSP [16] and MCDP [17] computer programs, respectively. Both methods evaluate the energy of the system using the same force field, which is based on the torsional, electrostatic, and van der Waals contributions. The torsional energy is described using a classical three-term Fourier expression,

$$E_{tor}(\varphi) = \sum_{n=1}^{3} \frac{V_n}{2}[1 + \cos(n\varphi - \gamma)] \tag{1}$$

where V_n is a force constant, *n* is the multiplicity factor, and γ is the phase angle. The van der Waals energy is computed in the usual pair-wise additive way using a Lennard-Jones 12-6 potential, which is only calculated between atoms of different chains or atoms in the same chain separated by at least three bonds.

$$E_{vdW} = \sum_i \sum_{j>i} \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \tag{2}$$

The electrostatic term is computed by applying the Coulombic expression:

$$E_{el} = \sum_i \sum_{i>j} \frac{q_i q_j}{4\pi\varepsilon_o \varepsilon_r r} \tag{3}$$

In the present study torsional and van der Waals parameters were taken from the Amber's set [12]. Atomic electrostatic charges were explicitly derived for each nylon *n* by fitting the rigorously defined quantum mechanical molecular electrostatic potential, which was calculated at the HF/6-31G(d) level on a reduced model constituted by two residues, to the Coulombic electrostatic potential. In order to consider the conformational dependence of the

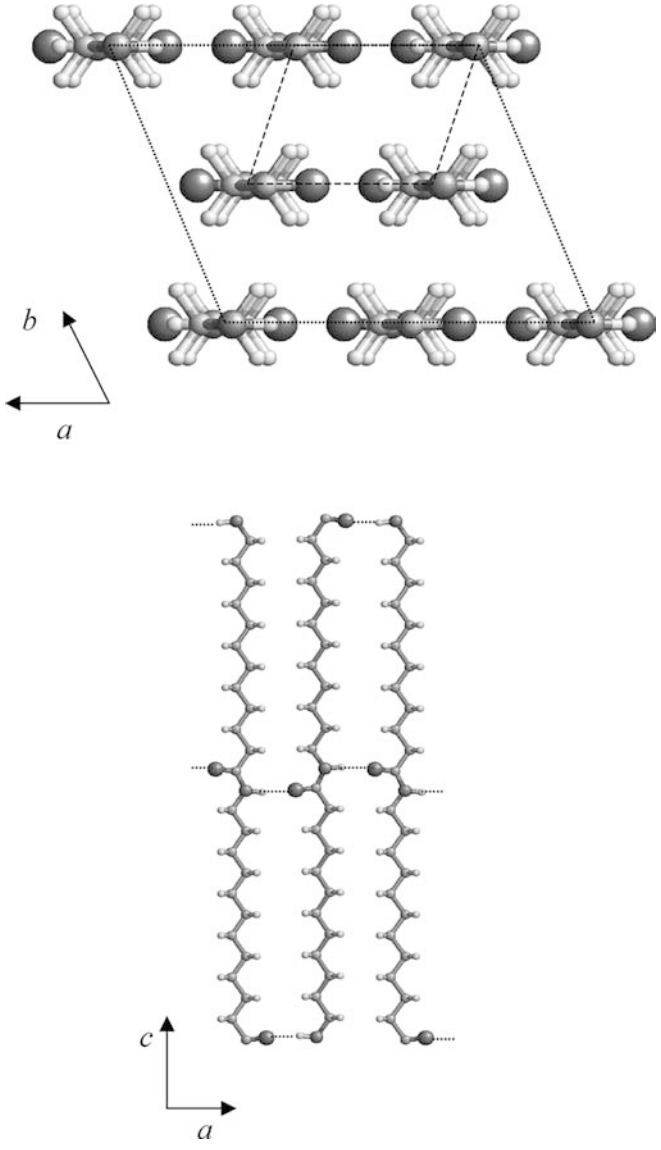

Fig. 1 Structure of the α form of nylon 12: unit cell (*dotted line*) projected along the *c*-axis (*top*) and hydrogen-bonded sheet made of antiparallel chains (*bottom*). The four chains explicitly considered in MC simulations are those belonging to the subunit cell (*dashed box*)

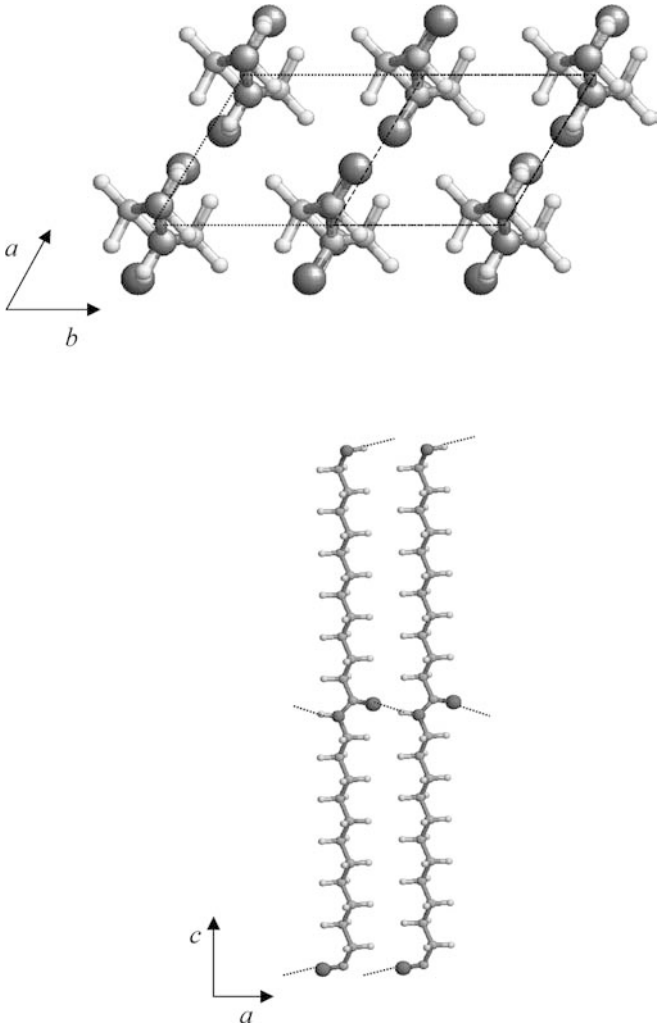

Fig. 2 Structure of the γ form of nylon 12: unit cell (*dotted line*) projected along the *c*-axis (*top*) and hydrogen-bonded parallel chains (*bottom*). The four chains explicitly considered in MC simulations are those belonging to the subunit cell (*dashed box*)

electrostatic parameters, the charges were computed using both the extended and quasi-extended conformations characteristic of the α and γ forms, respectively. Therefore, the electrostatic parameters were specifically computed not only for each nylon but also for each crystalline form (atomic charges are provided as supplementary material). Furthermore, it should be noted that, as is usual in the parametrization of the electrostatic term, intermolecular hydrogen bonds were not considered in this process. According to the recommendations given in the Amber force field [12], the nonbonding interactions within atoms of the same chain separated by exactly three bonds (1–4 interactions) were reduced by applying a 0.5 scale factor.

Pilot calculations on selected nylons *n*, i.e., typically $n = 6$ and 10, indicated that the α and γ structures are energy minima for the force field discussed in this section. Furthermore, these two structures are also energy minima when bond angles and distances are also considered as degrees of freedom. These results allow us to validate our force field and to check the influence of the restrictions imposed in the calculations (see below).

PCSP calculations

PCSP is a computer program specially designed to predict and analyze the packing in crystalline polymers through simple energy calculations [16]. Periodic boundary conditions were applied in the *a*-, *b*- and *c*-axes. A cutoff limit of 15 Å was chosen, implying that all atoms of one unit interact with all atoms of another unit if at least one pair of atoms is within the limit. In practice, this means that many interactions beyond the cutoff are taken into account as well. PCSP minimizes the energy of the system with respect to the setting angle, which defines the orientation of the chains linked by hydrogen bonds. However, energy minimizations with respect to the cell parameters and the chain positions within the cell are not

allowed by this computational strategy. In spite of this limitation, PCSP has been successfully used to study the crystal structure of odd–odd nylons *n*,*n* + *2* [18], nylon 46 [19, 20], nylons *n* 2 [21], and nylons *n* with *n* = 5 [22] and 6 [3].

MCDP simulations

MC simulations of the crystalline structures of even nylons *n* were performed considering four independent chains, which are indicated in Figs. 1 and 2. Chains were initially packed in a simulation box consistent with the crystallographic dimensions described previously. MC simulations of *NPT* type were performed at T = 298 K and P = 1 atm using the Metropolis algorithm [23]. The degrees of freedom in the simulations were: (i) the setting angle of the chains; (ii) the cell parameters *a* and *b*; and (iii) the position of the chains within the cell. Accordingly, molecular displacements along the *a*- and *b*-axes were combined with volume changes. The frequencies used for such types of moves were 30, 40, and 30%, respectively. Each simulation consisted of 2.5×10^5 steps, the atomic coordinates being saved every 2,500 steps. Periodic boundary conditions in the three axes and the minimum image convention were applied to all the simulations. Nonbonding interactions were neglected beyond 15 Å.

Results and discussion

Energy calculations

Figure 3 shows the variation of the energy difference between the α and γ forms ($\Delta E_{\alpha-\gamma}$) predicted by PCSP with respect to the value of *n* for even nylons. The γ was the favored crystalline structure in all cases, this trend being in full agreement with experimental observations for nylons 10, 12, and 18. The $\Delta E_{\alpha-\gamma}$ values displayed in Fig. 3 were computed with respect to the most stable model of the α form, which was that proposed by León et al. [3] for nylons 10 and 12, and by Holmes et al. [1] for nylons 18, 24, and 32. However, in all cases the energy difference between two such models was smaller than 25% of $\Delta E_{\alpha-\gamma}$, indicating that the stability of the γ form with respect to the α one remains unaltered from a qualitative point of view.

The profile displayed in Fig. 3 indicates that for nylons 10 and 12 the stability of the γ form suddenly increases with the size of the aliphatic segment. This is a reasonable result since, as the size of the aliphatic segment increases, the more efficient packing of the polymethylenic segments compensates for the poorer hydrogen bonding angle in the γ form, i.e., the hydrogen bonding geometries for the α and γ forms were [d(H···O) = 1.900 Å and > N–H···O = 175.6°] and [d(H···O) = 1.879 Å and > N–H···O = 164.9°], respectively. However, the stabilization provided by the incorporation of additional CH_2 groups is less pronounced for *n* > 12. Thus, the stability of the γ form increases by 2.3 kcal mol^{-1} $residue^{-1}$ when *n* changes from 10 to 12 (1.1 kcal mol^{-1} $residue^{-1}$ for each CH_2 group), while it increases by 2.2 kcal mol^{-1} $residue^{-1}$ when *n* changes from 24 to 32 (only 0.3 kcal mol^{-1} $residue^{-1}$ for each CH_2 group). An intermediate situation appears for the other nylons investigated. These results suggest that the importance of intermolecular hydrogen bonds in the relative stability of the two forms decreases with *n*.

Although this seems a reasonable result, it deserves more investigation due to the drastic approximations introduced in PCSP calculations. Thus, in spite of the reliability demonstrated by the PCSP method for studying the crystal structure of nylons with small aliphatic segments [3, 18, 19, 20, 21, 22], caution must be taken since the cell dimensions and the positions of the chains within the unit cell were kept fixed. Furthermore, entropic and thermal effects are neglected in energy estimations. In order to overcome these limitations, and to get a deeper insight into the relative stability between the α and γ forms of even nylons *n*, atomistic MC simulations were performed at room temperature.

Monte Carlo simulations

Energy profiles

MC simulations were performed for α and γ forms of the five nylons investigated. It should be mentioned that the simulations of the α form were performed using the most stable arrangement predicted by PCSP calculations as the starting geometry. Figure 3 includes the relative energies derived from MC simulations. As can be seen, the results obtained for nylons 10 and 12 are in excellent agreement with those derived from PCSP calculations. Thus, the γ form was the most favored for the two polymers, the $\Delta E_{\alpha-\gamma}$ being 4.3 kcal mol^{-1} $residue^{-1}$ larger for nylon 12 than for nylon 10. However, the behavior predicted for polymers with very large aliphatic segments is completely different from that provided by static energy calculations. Thus, $\Delta E_{\alpha-\gamma}$ decreases from

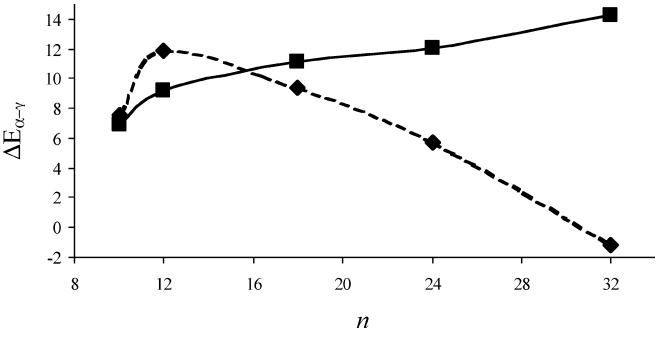

Fig. 3 Relative stability between the α and γ forms of nylons *n*. The energy (in kcal mol^{-1} $residue^{-1}$) of the α form relative to that of the γ form is represented vs. the value of *n*. The profiles were obtained using PCSP (■) and MCDP (◆) calculations

11.9 to 9.4 kcal mol^{-1} $residue^{-1}$ when n increases from 12 to 18, and to 5.7 kcal mol^{-1} $residue^{-1}$ for $n=24$. Moreover, for nylon 32 the α form becomes more stable than the γ one by 1.2 kcal mol^{-1} $residue^{-1}$. According to these results, the relaxation of both the cell parameters and the position of the chains within the cell seem to play a crucial role in even nylons n with very large polymethylenic segments ($n>12$). It should be noted that the differences between the PCSP and MCDP profiles cannot be attributed to the force field, since both the potential energy expressions and the parameters used by these methodologies were identical.

The present results indicate that the pseudohexagonal arrangement of the γ form provides an optimum packing of the aliphatic segments when the energy contribution provided by the intermolecular hydrogen bonds is significant, i.e., nylons 10 and 12. Moreover, when the contributions associated with the interactions between the amide groups are small but still not negligible, the γ form is still favored with respect to the α one, i.e., nylons 18 and 24. However, for very large aliphatic segments, i.e., nylon 32, MC simulations indicate that the packing of CH_2 groups is more efficient in the α form than in the γ form. Indeed, the energy profile derived from MC simulations can be easily rationalized by analyzing the geometry of the resulting structures. These analyses will be presented below.

Cell parameters

Table 1 shows the cell dimensions derived from MC simulations of *NPT* type for the α form of the five nylons under investigation. It is worth noting that the dimensions obtained for the nylons 10, 12, 18, 24, and 32 are very similar, the maximum difference with respect to the parameters experimentally observed for nylon 6 [1] being −0.22 Å, +0.16 Å, and −6.4° for a, b, and γ, respectively. These small variations with respect to the parameters used at the beginning of the simulations should be attributed to: (i) the force-field parameters used to evaluate the energy, which determine the optimum distance among different chains, and therefore the a and b parameters; and (ii) the geometric parameters used to build the chain, which affect the relative arrangement of the chains linked by hydrogen bonds, and therefore the γ angle. Figure 4a compares the evolution of the parameters a and b along the MC simulation for nylons 12 and 32. As can be seen, the cell parameters are satisfactorily converged after 2.5×10^5 MC steps.

Table 1 Crystal parameters[a] derived from MC simulations for the α form of even nylons n

	a	b	c	α	β	γ
Nylon 10	9.384	8.164	27.206	90.0	90.0	64.1
Nylon 12	9.391	8.178	32.201	90.0	90.0	64.3
Nylon 18	9.385	8.165	47.155	90.0	90.0	63.8
Nylon 24	9.385	8.149	62.110	90.0	90.0	64.0
Nylon 32	9.340	8.090	82.049	90.0	90.0	61.1

[a]Distances and angles in Å and degrees, respectively

The cell parameters predicted for the γ form are listed in Table 2. For nylon 10, the calculated cell axis dimensions were slightly larger (0.21 Å, 0.38 Å, and 4.5° for a, b, and γ, respectively) than the room crystallographic values [7]. Similarly, small differences appear when the parameters reported for nylon 12 ($a=4.79$ Å, $b=9.58$ Å, $c=31.9$ Å, and $\gamma=120°$) [14] are compared with the predicted ones. This is explained by the force-

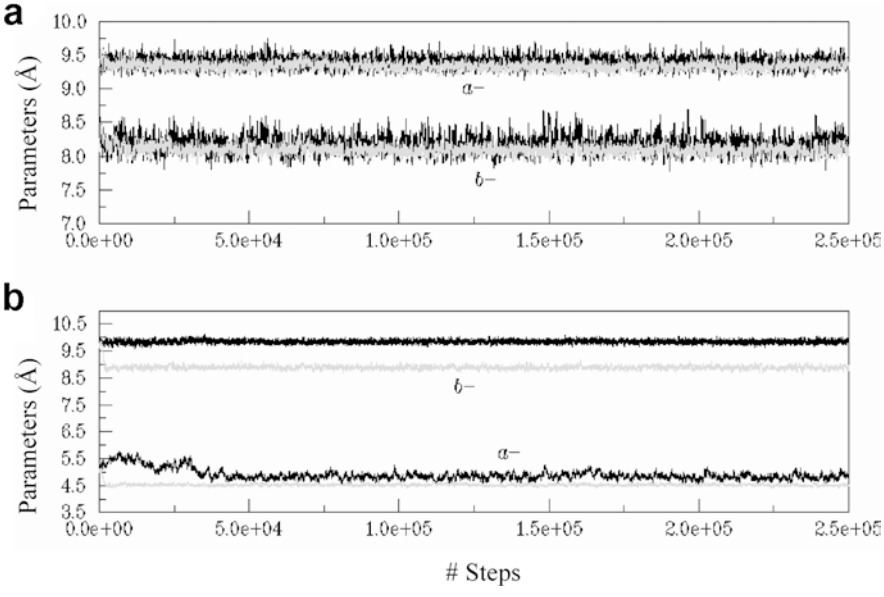

Fig. 4a, b Evolution of the cell parameters a and b through the *NPT* MC simulations for the α (**a**) and γ (**b**) forms of nylons 12 (*black lines*) and 32 (*gray lines*)

Table 2 Crystal parameters[a] derived from MC simulations for the γ form of even nylons *n*

	a	*b*	*c*	α	β	γ
Nylon 10	4.990	9.939	26.339	90.0	90.0	124.5
Nylon 12	4.840	9.844	31.534	90.0	90.0	119.8
Nylon 18	4.788	9.813	46.482	90.0	90.0	118.2
Nylon 24	4.692	9.756	61.450	90.0	90.0	109.0
Nylon 32	4.522	8.883	81.382	90.0	90.0	94.9

[a]Distances and angles in Å and degrees, respectively

field and geometric parameters used to generate the polymer chains, as for the α form. On the other hand, MC simulations predict a drastic reduction of the unit cell dimensions *a* and *b* when the number of CH_2 groups increases. Thus, such parameters decrease by 0.468 and 1.056 Å, respectively, when *n* changes from 10 to 32. Furthermore, the value of the angle γ gradually decreases towards 90° when the size of the aliphatic segment increases, the angle resulting for nylon 32 being 94.9°. These striking results indicate that the optimum distance between two packed CH_2 units is smaller when the contribution of the intermolecular hydrogen bonds is less important. This is consistent with the following experimental observation: no crystalline structure similar to the γ form of nylons has been identified for polyethylene and long paraffins. Accordingly, these results suggest that the γ form of even nylons *n* arises from the compromise between suitable packing of CH_2 groups and satisfactory hydrogen bonding geometries. Such compromise seems to provide a molecular organization that is the most stable when *n* ranges from 8 to ~30 but not for larger *n* values. The features described for nylon 32 are illustrated in Fig. 4b, which compares the evolution of the cell parameters *a* and *b* for nylon 12 and 32. The change of the angle γ will be detailed in the next sections.

Analysis of the chain positions in the α form

Figure 5 shows the positions occupied by the chains of nylon 12 and nylon 32 during the MC simulations of the α form. In both cases the molecules stay around their initial positions and do not move towards new positions. Thus, the monoclinic structure of the α form is clearly preserved during the whole simulation. However, a more detailed comparison between the results obtained for the two polymers indicates that the vibrations are considerably larger for nylon 12 than for nylon 32. This result is very surprising, since we expected that the larger size of the aliphatic segment would allow higher spatial fluctuations, since the importance of the intermolecular hydrogen bonds decreases. Moreover, examination of the setting orientation between the different chains reveals a consistent behavior. Figure 6a displays the evolution of the setting angle (θ) through the MC simulations for nylons 12 and 32. It is worth noting that the fluctuations of θ are considerably larger for nylon 12 (~20°) than for nylon 32 (~4°), even though the hydrogen bonds between adjacent chains within the sheet are maintained in both cases.

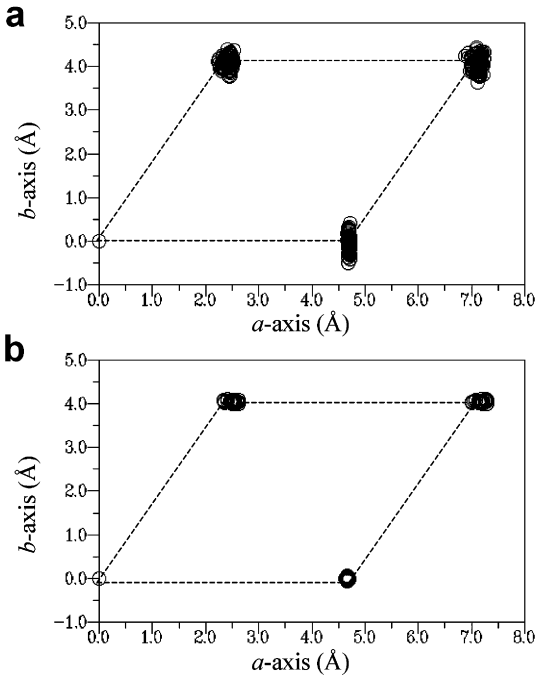

Fig. 5a, b Displacement (in Å) along the *a*- and *b*-axes of the nylon 12 (**a**) and nylon 32 (**b**) chains explicitly considered in the MC simulations of the α form. Displacements are computed with respect to the chain located at the origin. *Dashed lines* schematically indicate the subunit cell used in MC simulations

These results suggest that the interactions associated with the packing of methylene groups are more restrictive than the hydrogen bonds between amide groups. Thus, the stabilizing contribution provided by the hydrogen bonds, which are the dominating interactions for the shorter nylons, seems to be preserved even when the chains undergo considerable vibrations around the equilibrium positions. Conversely, the stabilization induced by the packing of the polymethylenic chains seems to be very sensitive to the vibrations of the chains. Accordingly, such movements are minimized for the nylons with very large aliphatic segments, in which the molecules essentially remain at their equilibrium positions. It should be emphasized that the results obtained for nylon 10 were very similar to those of nylon 12, while the motion of the chains for the other nylons investigated in this work decreases when *n* increases (data not shown).

Finally, we examined the variation of the shear of the sheets in the *c*-direction along the MC simulations. This

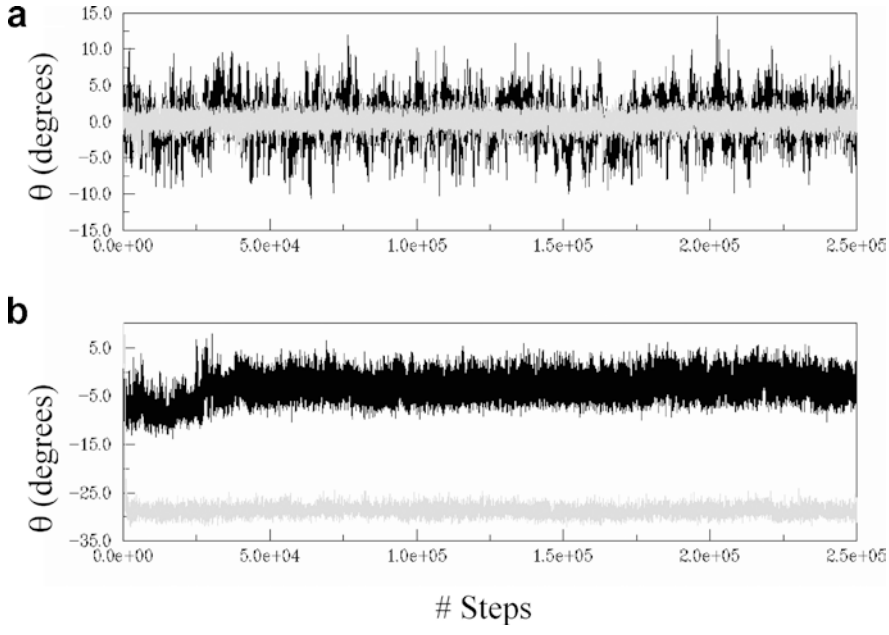

Fig. 6a, b Setting angle of nylon 12 (*black*) and nylon 32 (*gray*) as a function of the number steps: α form (**a**) and γ form (**b**)

is displayed in Fig. 7 for the α form of nylon 12. It is worth noting that Δc fluctuates between $3.5c/26$ and $5c/26$, suggesting a statistical arrangement similar to that proposed by León et al. for nylons 6 [3] and 46 [20]. Similar results were also obtained for nylon 10. On the other hand, Δc remains almost unaltered for nylons with very large aliphatic segments, i.e., $\Delta c \sim 3c/26$. This is consistent with the small vibrational motions described above for these polymers.

Analysis of the chain positions in the γ form

The motions of the molecules during the MC simulations are projected two-dimensionally in Fig. 8 for nylons 12 and 32. The chains of nylon 12 move around the equilibrium positions defined for the conventional γ form. Thus, the molecules spend most of their time vibrating around such positions, although rarely displacements of even $\sim$0.75 Å are detected along the *b*-axis. The hydrogen bonds between chains of adjacent sheets are preserved during such displacements since the two interacting chains move simultaneously in a concerted way. Inspection of Fig. 6b reveals that the fluctuations of the setting angle θ are consistent with these results. On the other hand, inspection of the shear displacement indicates that, as expected, Δc fluctuates around 0 (Fig. 7).

Figure 8b shows the positions occupied by the chains of nylon 32 during the MC simulations, while the evolution of the angle θ is displayed in Fig. 6b. It is worth noting that the polymer chains abandon their original positions very suddenly, the motions occurring after only a few MC steps as revealed by the change in θ.

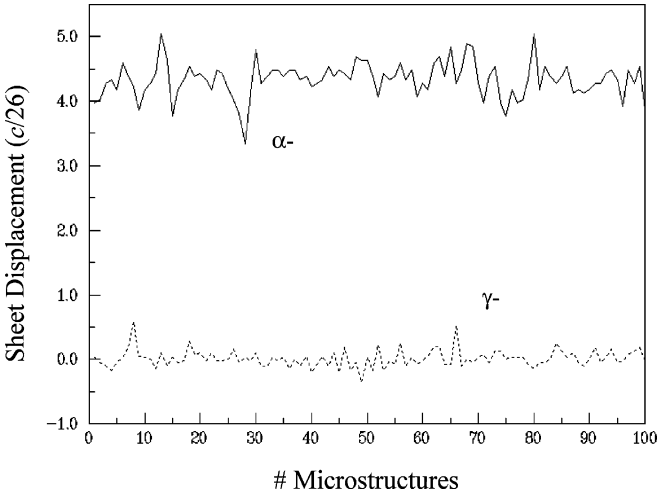

Fig. 7 Variation of the shear of the sheets in the *c*-direction along the MC simulations of nylon 12. *Solid* and *dotted lines* correspond to the α and γ forms, respectively

The more important characteristics of this fast structural change can be summarized as follows: (i) the chains move along both the *a*- and *b*-directions; (ii) the chains move concurrently in the same direction, as indicated by the notable reduction of the cell parameters *a* and *b*; and (iii) the angle γ evolves from 120° to $\sim$95°, which is consistent with a complete rearrangement of the chains.

These results allow us to conclude that the monoclinic lattice characteristic of the γ form does not provide the optimum packing for nylons with very large aliphatic segments. Thus, the energy of the system improves when the distance between the chains decreases, and the

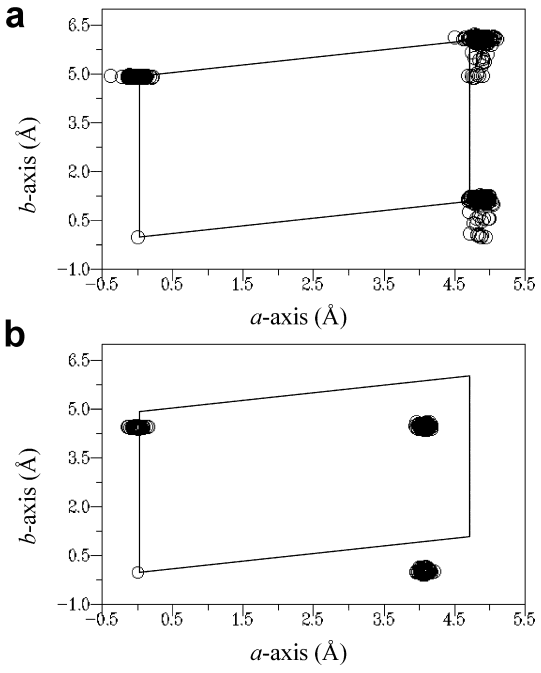

Fig. 8a, b Displacement (in Å) along the *a*- and *b*-axes of the nylon 12 (**a**) and nylon 32 (**b**) chains explicitly considered in the MC simulations of the γ form. Displacements are computed with respect to the chain located at the origin. *Dashed lines* schematically indicate the subunit cell used in MC simulations. The scale along the *a*- and *b*-axis is different

pseudohexagonal packing is abandoned. As a consequence, the intermolecular hydrogen bonding interactions are disrupted, which is consistent with the change in the setting angle. The energy penalty associated with the loss of the hydrogen bonds is overcome by the improvement in the packing of the CH_2 units. Figure 9 shows the structure resulting for nylon 32 at the end of the MC simulation. At this point, it should be remarked that we are not proposing a *new* crystal structure for nylons *n* with very large aliphatic segments, but we are showing the poor stability of the γ form for these polymers. This point will be specifically discussed in the next section. On the other hand, analysis of the results obtained for the other nylons indicates that the lattice of the γ form is preserved for nylon 18 while nylon 24 shows the same tendency as nylon 32, even though this is considerably enhanced in the latter polymer.

Significance and limitations of the computer experiments

Chemical synthesis and crystallization are undoubtedly among the more important difficulties to advance in the understanding of the nylons' structure. The study of high nylons is of interest to evaluate the influence that long aliphatic segments may exert on the molecular

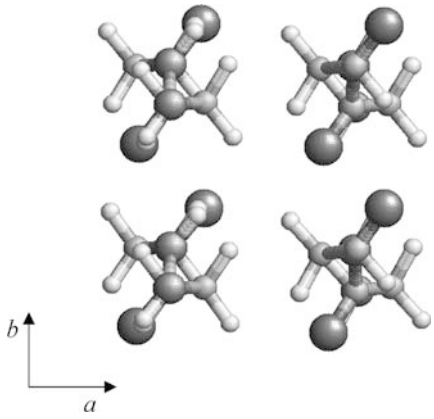

Fig. 9 Structure obtained at the end of the simulation of the γ form for nylon 32. The representation corresponds to the projection along the *c*-axis of the four chains explicitly considered in the MC simulation

arrangement. Thus, it is reasonable to think that the low density of hydrogen bonds present in these polymers may alter the molecular arrangement proposed for the conventional crystal forms of nylons. At this point suitable computer experiments may give some useful complementary information.

Much effort has already been spent on modeling polymer structure by means of computational methods. In this sense, atomistic MC and molecular dynamics simulations have proved to be especially useful. However, because of finite computer resources, computer simulations can only cover partial aspects. Moreover, the study of chemical and physical properties involving complex macromolecules is often not possible without reducing the degrees of freedom of the system. This is achieved by imposing severe restrictions, which allow reduction of the required computational power.

In this work we have investigated the stability of the conventional α and γ forms in nylons with very large aliphatic segments using atomistic MC simulations. For this purpose, independent polymer chains were allowed to move within the simulation box. However, in order to increase the efficiency of our simulation we imposed two severe restrictions: (i) the conformation of the polymer chain was kept fixed during the whole simulation; and (ii) the number of independent chains was only four. It should be noted that the investigation of structural transitions with these limitations is absolutely impossible since these are large-length scale transformations. Phase transitions involving important structural rearrangements can only be covered by considering a large number of independent chains and allowing conformational rearrangements. Although the restrictions discussed above are necessary to reduce the computational resources required in the present study, we have evaluated their impact on the results by performing some additional calculations for nylon 10. The insights

provided by such calculations can be summarized as follows: (i) complete geometry optimizations, i.e., without restrictions, indicated that the α and γ forms are energy minima; (ii) no significant change is observed in the MC results when the dihedral angles are considered as degrees of freedom.

According to the previous considerations, the results obtained in the present work allow us to conclude that the conventional γ form is not stable for nylons *n* with very large aliphatic segments. Thus, the density of hydrogen bonds is so low that the packing is governed by the interactions between CH_2 units, which induce a complete structural transformation. It should be remarked that the arrangement achieved for nylon 32 at the end of the simulations of the γ form is not proposed as the result of such structural transition. Indeed, there is no physical meaning in this structure since it was obtained through restricted MC simulations. On the other hand, the conventional α form was very stable for nylon 32, as was indicated by the tendency of polymer chains to remain around the equilibrium positions. Moreover, the α form was energetically more favored than the structure resulting from simulations of the γ form. However, other structural arrangements not investigated in this work could be even more stable than the α form.

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