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Structure of the Extended Crystal Forms of Nylon-6

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Two crystal forms, α and β, were originally described by Holmes et al.[1] for nylon-6 with chains in an all-trans conformation, the former being the most frequently observed. In both forms, hydrogen-bonded sheets made of antiparallel chains are progressively shifted 0.153 nm along the a-axis (hydrogen-bonding direction). These authors proposed for the α-form a monoclinic lattice with sheets sheared in a recuperative manner along the c-axis (chain axis). The β-form distinguished from the α-form in that the c-shear is progressive leading to a triclinic structure. Both forms have the same unit subcell when projected down the c-axis with $a = 0.478$ nm, $b = 0.400$ nm, and $\gamma = 67.5°$. Whereas the shifting distance of the sheets along the a-axis could be firmly and exactly established from evidence provided by X-ray diffraction, the same cannot be said about sheet displacement along the c-axis. Nevertheless, a shearing distance of $\Delta c = 3c/14$ units, i.e., 3 averaged main chain bonds, was proposed for these two forms. The uniform distribution of amide groups in the space and the alternated arrangement of the *zigzag* polymethylene segments resulting from such a displacement were claimed to be advantageous features of the proposed structures.

Although the structure of the extended crystal forms of nylon-6 have been reexamined by a number of authors,[2−6] the original packing models put forward by Holmes et al.[1] have remained essentially unchanged. On the other hand, it is still unclear, when and in what proportion, α- and β-forms coexist in nylon-6 samples. Whereas these two forms may be clearly distinguished from the slightly contracted γ-form (the third crystal form known for nylon-6) by both X-ray[7] and CP-MAS NMR[8] spectroscopy, discrimination between themselves is much more difficult by experimental techniques. In this work we reinvestigate the crystal structure of nylon-6, employing several computational tools in combination with reported X-ray diffraction data.[1,3] The energy of the possible structures has been estimated with the PCSP computer program[9,10] using three independent force fields explicitly developed for simulation of nylon polymers.[6,10,11] The four investigated structures are those obtained by combining the arrangements shown in Figure 1 for the side-by-side packing of the hydrogen-bonded sheets along the a-axis (**I** and **II**) and along the c-axis (α and β).

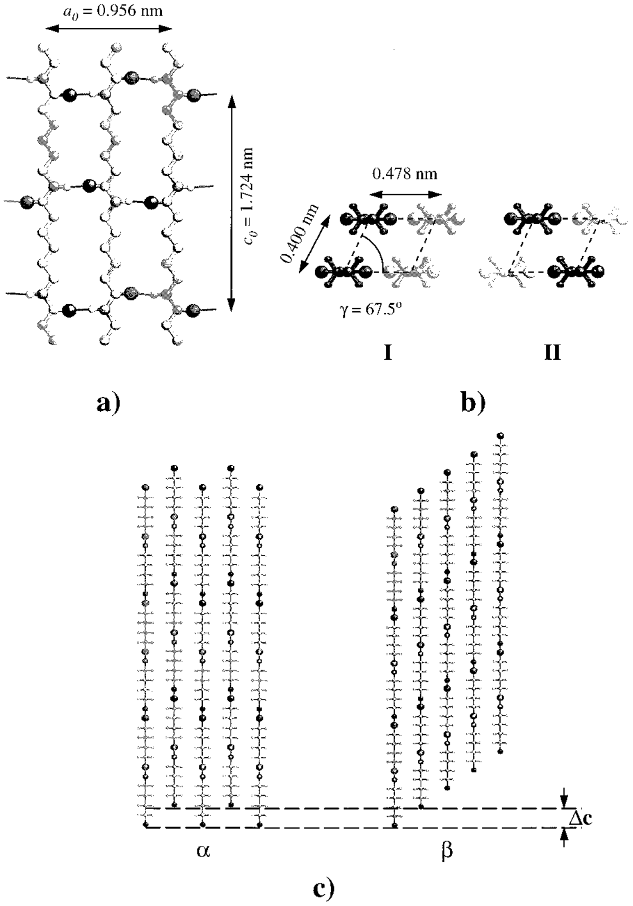

Figure 1. Possible arrangements for the crystal packing of nylon-6 chains in the fully extended conformation: (a) hydrogen-bonded sheet made of antiparallel chains; (b) nylon-6 subunit cell projected down the c-axis; (c) view of the hydrogen-bonded sheets projected along the a-axis.

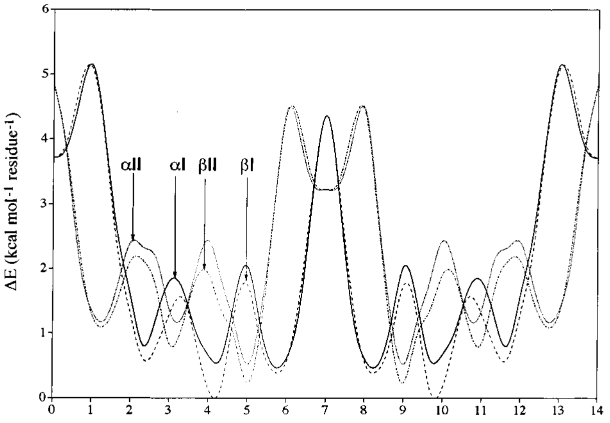

Figure 2. Relative energy vs Δc displacement for the four structures possible for the extended crystal forms of nylon-6. Note that the projected basal structure is the same for the four cases and that it does not varies with Δc.

The results provided by the three force fields were almost undistinguishable, indicating an excellent agreement among them. Figure 2 shows the profiles obtained with one of such force fields, which represents the energy of the crystal against Δc for the four possible structures. The extent of the displacement is expressed as $c/14$ units, and the energy is referred to one chemical residue. The four traces are symmetrical with respect to $c/2$, indicating that the shearing along the c-axis is independent of the sense of the displacement. It is observed that all the arrangements in which the amide

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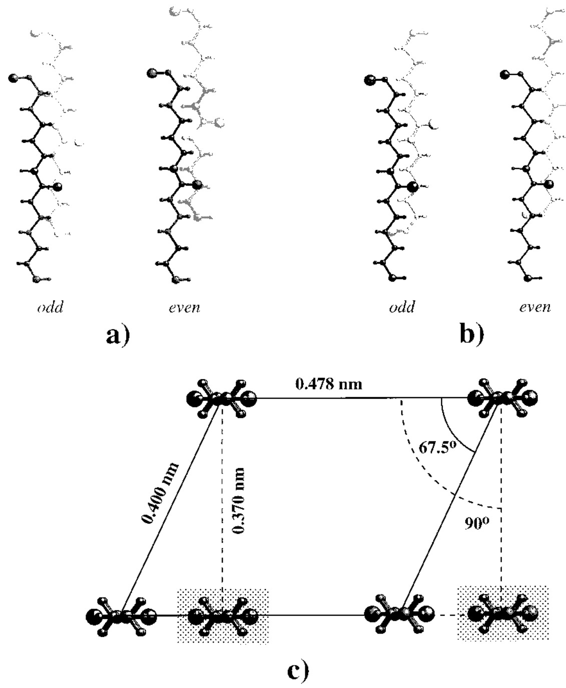

Figure 3. Relative position between the nearest chains belonging to adjacent sheets for arrays **I** (a) and **II** (b) for an odd (3) or even (4) number of *c*/14 units displacement. The arrangement may be eclipsed or alternated for either type of displacement depending on the array that is adopted. The relative stability of the eclipsed and alternated arrangements is determined by the geometry of the lattice (c).

groups are located close in the space, i.e., those with displacements near to *c* and *c*/2, appear to be energetically disfavored. Conversely, a low-energy region containing local minima for the four structures with an energy surplus smaller than ~1 kcal mol^{-1} residue^{-1} spans from 2*c*/14 to 6*c*/14. The absolute energy minimum corresponds to the β**I** structure with $\Delta c \sim 4c/14$. It is worth noting that similar trace shapes are obtained for α**I** and β**I** structures. Furthermore, the energy differences between these two forms never exceed 0.5 kcal mol^{-1} residue^{-1}, their profiles being almost isoenergetic within a considerable interval of displacements.

All minima found for arrangement **I** are located at even numbers of *c*/14 units whereas those for arrangement **II** appear for odd values. This result can be rationalized taking into account how the displacement along the *c*-axis modifies the spatial relationship between nearest chains belonging to neighboring sheets. At even values of Δc, these chains are in eclipsed (uncrossed) or alternated (crossed) arrangement for arrays **I** and **II**, respectively (Figure 3). The opposite situation results for displacements involving odd values of Δc. In fact, both quantum mechanical[12] and force-field calculations revealed that preference for a specific arrangement is determined by the geometry of the lattice. Thus, the alternated arrangement is the most favorable one only when the lattice is orthogonal ($\gamma = 90°$), which is the not the case for nylon-6 or other closely related nylons. For the nonorthogonal geometry of nylon-6 ($\gamma \approx 65°$), the eclipsed arrangement is largely preferred, which is contrary to predictions formulated by Holmes et al.[1] This result is in agreement with the structure adopted by certain *n*-alkanoamides which have been recently investigated in connection with the structure of nylons.[13]

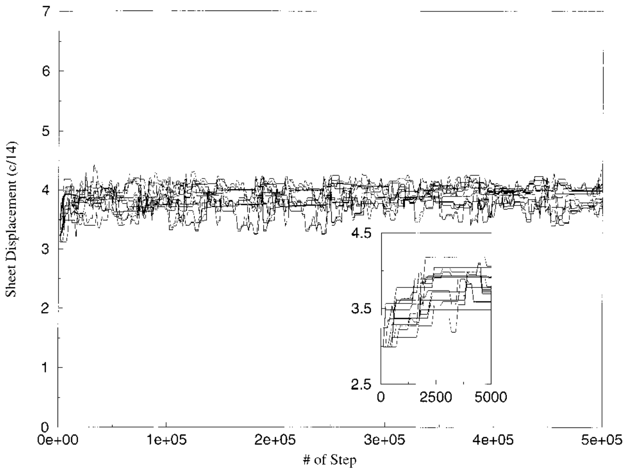

Figure 4. Variation of the shear of the sheets in the *c* direction along the MC simulation. The starting structure was α**I** with a displacement along the *c*-axis of 3*c*/14 units. At the earlier stages of the process there is a fast evolution toward an arrangement with a sheet displacements of about *c*/14 units (inset).

To support the results provided by PCSP calculations, Monte Carlo (MC) simulations[14] of an infinite crystal of nylon-6 were performed using as starting geometry the structure proposed by Holmes et al.[1] for the α-form in arrangement **I**, i.e., with $\Delta c = \pm 3c/14$. Figure 4 shows the evolution of Δc along the course of the simulation process. An abrupt change in the trajectory was found to take place after a relative small number of simulation steps, the initial sheet displacement increasing up to 4*c*/14. Similar results were obtained when MC simulations were carried out using the β**I** model as the starting structure.

As a final step of this study, we investigated the suitability of the low-energy structures of nylon-6 to reproduce the experimental X-ray diffraction reported by different authors.[1,5] For this purpose, all the arrangements corresponding to minima displayed in Figure 2 with a relative energy lower than 1 kcal mol^{-1} residue^{-1} were modeled and their respective fiber diffraction patterns simulated using the Cerius^2 program.[15] An excellent agreement between simulated and experimental data was found for all the models with calculated *R*-factors ranging from 21% to 23%. The conclusion drawn from this study is that no discrimination among the different structures feasible for nylon-6 can be made on the basis of X-ray diffraction data.

Since energy differences between the minima predicted from PCSP calculations are very small, a statistical structure may be adequate to represent the crystal structure of nylon-6 with chain in fully extended conformation. Such structure would be comprised of a mixture of α- and β-forms in both **I** and **II** arrangements with sheets displaced at definite Δc values ranging from 2*c*/142 to 6*c*/14. The contents in the different arrangements are estimated to vary from ~3% for the α**II** at 3*c*/14 up to ~22% for the β**I** at 4*c*/14.[16] The mixed structure would be compatible with all reported X-ray diffraction data. A similar type of statistical model has been recently proposed for the crystal structure of both nylon-46[16] and nylon-5.[17] It is reasonable to think, however, that such a highly heterogeneous structure only would come into existence under sudden crystallization conditions; otherwise, the lowest energy structure β**I** with successive sheets displaced four main chain atoms along the *c*-axis would be preferred.

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