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Measurement of the Intersheet Shear Along the Chain Axis in Nylon 6

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ABSTRACT: X-ray and electron diffraction studies on solution-grown crystals of high-fidelity, monodisperse nylon 6 oligoamides have provided the opportunity to measure, by experiment, the intersheet chain-axis, or *c*-axis shear (Δc). For almost 50 years this Δc value for the classical α-structure of nylon 6 has been taken, by analogy with nylon 6 6, to be 0.37 nm. Our evidence suggests that the Δc value is likely to be 0.14 nm and certainly lower than 0.21 nm. In addition to crystallizing the 5-amide nylon 6 oligomer in the alternating intersheet-sheared α-structure, we have crystallized this monodiperse oligomer in the progressively intersheet-sheared λ-structure. In this structure we find that $\Delta c = 0.35$ nm, a value we have also independently discovered for the λ-structure of nylon 8. Modeling the intersheet interaction energy, as a function of incrementally changing Δc, gives two Δc values: 0.14 and 0.36 nm. These values closely match our experimental results.

Introduction

Two crystalline structures, α and β, for the aliphatic polyamide $[\mathrm{NHCO(CH_2)_5}]_n$, or nylon 6, were described by Holmes et al.[1] in 1955. In both structures the polar chains exist in the all-trans, flat-ribbon conformation with neighboring antiparallel chains hydrogen bonding together to form flat sheets (*ac*-plane) with the chain direction along the *c*-axis and hydrogen bond direction parallel to the *a*-axis. A third crystalline phase, the γ-structure,[2,3] where the amide units twist out of the all-trans conformation is not of relevance in this present contribution. In the α- and β-structures, the sheets stack via van der Waals interactions[4] with progressive shear (shear angle, $\gamma = 112.5°$) parallel to the *a*-axis. In addition, there is *c*-axis intersheet shear, and in this specific aspect the structures differ. In the more common and stable α-structure (Figure 1a), the *c*-axis shear, measured as a fraction (Δc) of the crystallographic *c* value, was found to be regularly alternating; i.e., there was no progressive shearing effect along the chain axis, and Δc was chosen to be $3c/14$, or 0.37 nm.[1] The estimation of this *c*-axis shear has to rely on accurate intensity measurements of (principally) the 00*l* diffraction signals. In practice this is not possible, because the intensities are inherently weak (therefore, poor signal-to-noise ratio) for the α-structure owing to the alternating *c*-axis intersheet shear. Thus, only limits to the range of Δc values can be realistically imposed.[5] In the nylon 6 α-structure,[1] it would appear that the $\Delta c = 0.37$ nm value was taken from the structure of nylon 6 6.[6] Although the nylon 6 6 structure[6] has essentially the same crystallograghic *c* value as nylon 6,[1] it is obviously quite a different polymer, in both stereochemistry and crystal structure. In short, the value of $\Delta c = 0.37$ nm chosen for nylon 6 β-structure (Figure 1a) was an estimate.[1] The nylon 6 β-structure[1] was thought to have a value of $c \simeq 0$ (a rough estimate based on the observed strong relative intensity of the 002) or that it was composed of sheets containing nonlinear hydrogen bonds and possible perturbations from the all-trans chain conformation; in essence, the β-structure[1] was not well defined. Thus, perhaps surprisingly, after nearly 50 years there has been no direct measure of the Δc intersheet shear value for nylon 6 or related even nylon structures.[7]

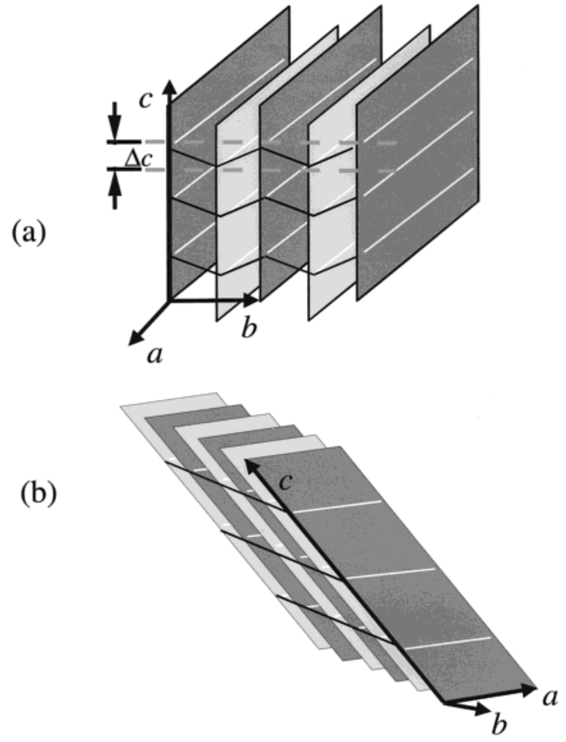

Figure 1. Schematic views of the nylon 6 structures. The shaded planes represent the hydrogen-bonded sheets (*ac*-planes); white lines, hydrogen bond direction; black lines highlight the nature of the shear. (a) α-Structure with alternating *c*-axis intersheet shear; magnitude given by Δc. (b) Progressive intersheet-sheared λ-structure.

Recently, we have been studying nylon 6 structures using high-fidelity, monodisperse oligoamides[8−12] and have crystallized the 5-amide oligomer in two distinct crystalline phases. The first phase is the same as the usual nylon 6 α-structure, with alternating intersheet *c*-axis shear, but with an important additional feature: the short molecules (4.60 nm long) making up the α-structure also stack in the chain direction (*c*-axis) with

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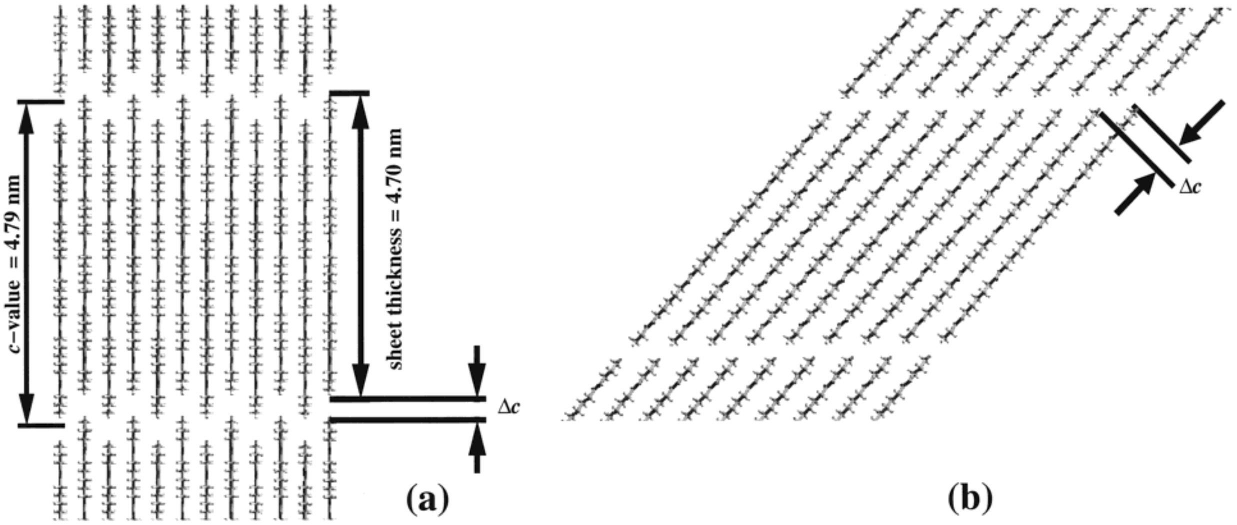

Δc ≤ 0.21 nm

Δc = 0.35 nm

Figure 2. Projections, parallel to the *a*-axis, of the 5-amide nylon 6 crystals: (a) α-structure; (b) λ-structure. Note that the sheet thickness is 0.1 nm larger than the molecular length of 4.60 nm.

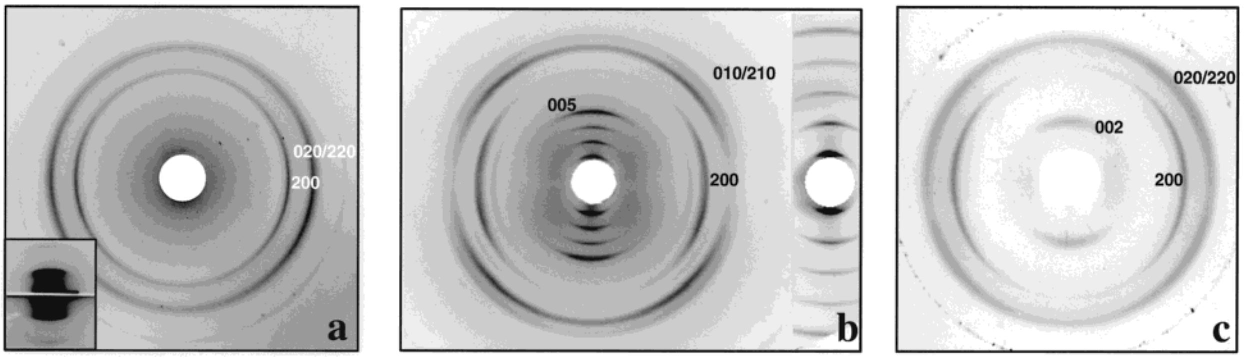

Figure 3. X-ray diffraction patterns of sedimented mats; beam parallel to mat surface and mat normal vertical. (a) α-structure of the 5-amide nylon 6 oligomer.[9] The wide-angle signals are the $d_{200} = 0.44$ nm and $d_{020/220} = 0.37$ nm interchain diffraction signals. Two orders of the lamellar stacking periodicity (LSP) with spacing 4.79 nm occur on the meridian; first order shown in inset. (b) λ-structure of 5-amide nylon 6. The LSP value is 3.31 nm in this case owing to severe progressive *c*-axis intersheet shear. Inset shows the LSP in more detail, including the first order. (c) λ-structure in chain-folded nylon 8 lamellar crystals. The spacing of the 002 meridional arc gives a direct measure of the progressive *c*-axis intersheet shear.

crystallographic precision to form a three-dimensional crystal (Figure 2a). The results enable us to obtain a direct measure for the maximum value of Δ*c* for the α-structure. We hasten to add that we have additional information regarding *c*-axis intersheet shear for nylon 6. In the second crystalline phase, that we have obtained for the 5-amide nylon 6 oligomer, the *c*-axis intersheet shear, Δ*c*, is *progressive* (Figure 1b) rather than alternating. In this recently discovered[10,11] λ-structure (Figure 2b), the magnitude of Δ*c* is different. We have also identified this new λ-structure, for a chain-folded polymer, as shown in the X-ray diffraction pattern from the nylon 8 polymer (Figure 3c)[13] and are currently in the process of attempting to obtain the λ-structure for the nylon 6 polymer. It is possible to obtain a direct experimental measure of Δ*c* for the λ-structure.

Measurement of the *c*-Axis Intersheet Shear (Δ*c*). 5-Amide Nylon 6 α-Structure. This relatively short (4.60 nm) nonfolded nylon 6 oligomer crystallizes in the form of three-dimensional crystals, where layers of molecules (lamellae) are in crystallographic register in the *c*-direction,[14] as shown in Figure 2a, and the crystal thickness is much greater (>×20) than the length of the molecule. The X-ray diffraction pattern, taken with the incident beam orthogonal to the coincident *c*,*c**-direction, is shown in Figure 3a. The diffraction signals index on a four-molecule monoclinic unit cell with parameters:[9] $a = 0.970 \pm 0.002$ nm; $b = 0.805 \pm 0.002$ nm; $c = 4.79 \pm 0.02$ nm; $\alpha = \beta = 90°$; $\gamma = 114°$. These values match the usual nylon 6 α-structure, except of course for the *c* value (chosen in nylon 6[1] to be 1.724 nm[14]). The lamellar stacking periodicity (LSP) gives rise to a series of orders of 4.79 nm (Figure 3a) along the meridian in the X-ray diffraction pattern. The maximum value of the alternating Δ*c* intersheet shear can be computed from the difference between this 4.79 nm LSP value and the sheet thickness, as illustrated in Figure 2a. However, clearly there is some uncertainty with respect to the degree of interdigitation between sucessive layers. As a consequence, we are only able to establish beyond doubt the maximum value for Δ*c*, which is 0.21 nm. Thus, Δ*c* for the α-structure of the 5-amide nylon 6 crystals is $\leq 0.21 \pm 0.04$ nm, a value significantly lower than the accepted figure of 0.37 nm.[1]

5-Amide Nylon 6 λ-Structure. In this progressively intersheet *c*-axis sheared structure (Figure 2b), Δ*c* can be measured directly from the X-ray diffraction pattern shown in Figure 3b, obtained with the incident beam orthogonal to the c^*-axis. The diffraction signals index on a two-molecule triclinic unit cell with the following parameters:[15] $a = 0.967 \pm 0.002$ nm; $b = 0.540 \pm 0.002$ nm; $c = 4.56 \pm 0.02$ nm; $\alpha = 49.3°$; $\beta = 90°$; $\gamma = 71.4°$. A series of meridional diffraction signals, orders of the LSP = 3.310 nm spacing, are evident in Figure 3b.

The unit cell parameters were derived from ≈40 *hkl* diffraction signals measured from both X-ray and electron diffraction patterns. From the crystallographic angles the chain tilt (c^c^*) was computed to be 43.5 ± 1°,[16] allowing us to calculate the Δc value with confidence. The X-ray diffraction data gives an intersheet spacing, d_{010}, = 0.370 ± 0.002 nm. The intersheet shear can be calculated using the relation:

$$\Delta c = d_{010} \tan(c^\wedge c^*)$$

and the value of Δc was found to be 0.35 ± 0.02 nm for the λ-structure. The quality of the X-ray diffraction data for this 5-amide λ-structure is also sufficiently good to confirm the value for Δc based on nylon 6 polymer sublattice.[14] Some of the *hkl* wide-angle diffraction signals could be indexed on the polymer sublattice with the same crystallographic parameters except for c, which was found to be 1.724 nm. Thus, the ratio of this sublattice c value to the calculated d_{002} (=0.620 nm) provides a second method of determining the tilt angle (c^c^*) and confirms our Δc value of 0.35 ± 0.02 nm calculated above.

The progressive intersheet-sheared λ-structure bears a similarity to the nylon 6 6 progressive intersheet-sheared α-structure. The progessive-sheared nature in both cases allows a direct measure of Δc.[6,17]

Why Two Δ*c* Values?

Using molecular modeling of the sheets and intersheet energy calculations, we are in a position to offer an explanation for the two different Δc values found in the 5-amide nylon 6 λ- and α-structures. In outline, the strategy and procedure are as follows. Adjacent sheets are translated parallel to the c-direction by incremental values of Δc. For each starting value chosen, the structure is allowed to relax, i.e., the potential energy allowed to minimize, subject to the constraints dictated by the experimental data (e.g., measured intersheet separation value, etc.), and consequently Δc is allowed to drift so that the whole structure settles into a local energy minimum.[18] The modeling procedure used allowed us to locate values of Δc where the interaction energy between atoms within the crystal lattice is at the (local) mimimum. Only energy minima which fell within the Δc region determined by experiment were of interest. The calculated energy profile is illustrated in Figure 4.

The software package Cerius 2, version 3.8 (MSI) was used in the structural modeling. First structures were built for different starting values of Δc, and the value was changed incrementally. Energy minimizations ($E_{\min}$) using the CVFF force field and crystallographic periodic boundary conditions were then performed for each Δc value and the molecular conformation and unit cell parameters allowed to alter. This enabled the localized energy minimum to be found. No serious departures from the usual nylon 6 sheet structure occurred, and in all cases the final models were found to be in the standard nylon 6 hydrogen-bonded sheets with the normal intersheet distance and a-axis intersheet shear. It should be noted at the outset that, in the case of the λ-structure, if Δc is changed the unit cell angles α and γ will also change; however, the value of the reciprocal angle γ^* must be conserved. This means that when the Δc value for the progressively sheared λ-structure is changed, the γ-angle must be automatically adjusted for each value of α. For the triclinic progressively sheared λ-structure,[11] $\gamma^* = 114.9°$.[16]

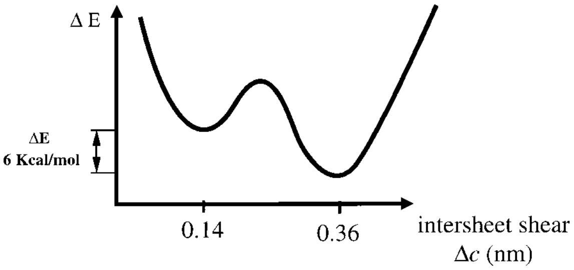

Figure 4. Energy profile showing the two minima at Δc = 0.14 and 0.36 nm.

For both progressive (λ-like) and alternating (α-like) c-axis intersheet shears, two energy minima were found, as shown in Figure 4. Interestingly, in both cases, the energy profile has the same key features. When the initial incremental Δc values were chosen in the range of $0.00 \le \Delta c \le 0.25$ nm the final Δc value converged to 0.14 nm. When the initial incremental Δc values were chosen to be greater than 0.25 nm,[20] Δc converged to a different minimum, at $\Delta c = 0.36$ nm. The first Δc value, at 0.14 nm, falls below the maximum allowed value of $\Delta c = 0.21$ nm found by experiment in our α-structure, which is reassuring. The latter Δc value of 0.36 nm matches well the value found experimentally in the 5-amide nylon 6 λ-structure, and the room-temperature value of $\Delta c = 0.353$ nm for nylon 8.[13,21]

The discovery of the two separate minima suggests that Δc in alternatingly sheared α-structure and progressively sheared λ-structure might be different. In the case of progressive shear, Δc does not influence the surface smoothness and so larger shears do not increase the surface energy. However in the α-structure, the surface energy is more closely related to Δc since lower shear values provide smoother surfaces and therefore lower surface energies. The calculated Δc values are in good agreement with those observed experimentally for the nylon 6 α- and λ-structures. We should note, in passing, that Leon et al.[19] reported some potential energy calculations associated with the intersheet shear in nylon 6. Rigid-body sheets were Δc shifted and the potential energy values plotted. Not surprisingly, numerous energy minima, corresponding to the anticipated atomic fluctuations for the interaction energy between rigid sheets, were generated. These potential energy plots appear to us to bear little relationship to the mechanism for real intersheet shear in nylon 6, or to our experimental results from the 5-amide oligomers.

Conclusions

X-ray diffraction and electron microscopic evidence from lamellar crystals obtained from 5-amide nylon 6 oligomers show that the c-axis intersheet displacement, Δc, differs between the α-structure, with alternating Δc shear, and the λ-structure, with its progressive intersheet shear. Realistic potential energy calculations, coupled with molecular modeling, suggest that there are two possible intersheet energy minima, at 0.14 and 0.36 nm, respectively, as a function of Δc. Similar energy profiles were obtained for nylon 6 crystal structures with both progressive and alternating *c*-axis intersheet shear. The first minimum, at $\Delta c = 0.14$ nm, occurs in the alternating intersheet sheared nylon 6 α-structure. This Δc value is different from the value of 0.37 nm suggested by Holmes et al.[1] in 1955, which has tended to be universally accepted for almost half a century. The second minimum, found experimentally at $\Delta c = 0.35 \pm 0.02$ nm, occurs in our recently discovered progressive intersheet-sheared λ-structure[10,11] and in nylon 8.[13] Thus, these two Δc values are wholly in agreement with the experimental values for our monodisperse nylon 6 oligomers.

Studies on these high-fidelity monodisperse nylon 6 oligoamides have provided the first direct measurement of the *c*-axis intersheet shear for nylon 6, and the results do not support the originally suggested value for the α-structure of the nylon 6 polymer.[1]

Finally, it should be noted that the λ-structure is not wholly associated with nonfolded monodisperse nylon 6 oligoamides. We have also identified the λ-structure in chain-folded lamellar crystals of nylon 8 polymer[13,21] and are currently looking for it in the nylon 6 polymer.

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References and Notes

(1) Holmes, D. R.; Bunn, C. W.; Smith, D. J. *J. Polym. Sci.* **1955**, *17*, 159.

(2) Arimoto, H.; Ishibashi, M.; Hirai, M.; Chantani, Y. *J. Polym. Sci., A* **1965**, *3*, 317.

(3) Salem, D.; Weigmann, H. *Polym. Commun.* **1989**, *30*, 336.

(4) Arridge, R. G. C.; Cannon, C. G.; *Proc. R. Soc. London* **1964,** *278*, 91. In this paper, calculations of the dipole−dipole interaction energy showed that the contribution of the hydrogen-bonded sheet interacting with its two neighboring sheets add only about 5% (0.48 kcal/mol ≪ 2.5 kcal/mol (*kT*)) to the total dipole−dipole interaction energy (9.6 kcal/mol) in the nylon 6 6 crystal lattice. As a consequence, the value of the intersheet shear, Δc, is essentially a result of the intersheet van der Waals interactions.

(5) We estimate that for the nylon 6 α-structure the limits in Δc are $0.1 \text{ nm} < \Delta c < 0.45$ nm, and the chosen value of $\Delta c = 0.37$ nm taken from nylon 6 6 is within these limits.

(6) Bunn, C. W.; Garner, E. V. *Proc. R. Soc. London* **1947**, *189*, 39.

(7) Energy profiles can, of course, be calculated, but it must be remembered these are impirical calculations and are not in the same category as a direct experimental measurement.

(8) Cooper, S. J.; Atkins, E. D. T.; Hill, M. J. *J. Polym. Sci. Polym. Phys.* **1998**, *36*, 2849.

(9) Cooper, S. J.; Atkins, E. D. T.; Hill, M. J. *Macromolecules* **1998**, *31*, 5032.

(10) Cooper, S. J.; Atkins, E. D. T.; Hill, M. J. *Macromolecules* **1998**, *31*, 8947.

(11) Atkins, E. D. T.; Hill, M. J.; Jones; N. A.; Sikorski, P. *J. Mater. Sci.* **2000**, *35*, 5179.

(12) The chemical synthesis of these monodisperse oligoamides were undertaken by Dr. G. Brooke and his colleaugues at the Chemistry Department, University of Durham (see: Brooke, G. M.; Mohammed, S.; Whiting, M. C. *Chem. Commun.* **1997**, *16*, 1511; Brooke, G. M.; Mohammed, S.; Whiting, M. C. *J. Chem. Soc., Perkin Trans 1* **1997**, *22*, 3371. Brooke, G. M.; Mohammed, S.; Whiting, M. C. *Polymer* **1999**, *40*, 773. Brooke, G. M.; MacBride, J. A.; Mohammed, S.; Whiting, M. C. *Polymer* **2000**, *41*, 6457) in response to a desire by Prof. E. Atkins and his colleagues at the Physics Department, University of Bristol, for high-fidelity oligoamides and polyamides that were deemed necessary for studying fundamental aspects in polymer physics. We thank the Engineering and physical Sciences Research Council, U.K., for supporting this collaborative work.

(13) Jones, N. A.; Sikorski, P.; Atkins, E. D. T.; Hill, M. J. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 3302.

(14) The X-ray diffraction patterns shown in Figures 3a,b, were obtained by sedimenting the monodisperse 5-amide nylon 6 crystal flakes. Each flakelike crystal consists of many lamellae (≈a few nanometers thick) stacked in crystallographic register along the c^*-direction. On sedimentation, the crystals settle with random azimuthal rotation (about the c^*-axis or lamellar normal (meridian in Figure 3)). Thus, the intralamellar (sublattice) nylon 6 structure is sampled by planes of reciprocal spacing $1/\text{LSP nm}^{-1}$. This spacing is not an integer multiple of the intralamellar (sublattice) structural repeat, i.e. the usual all-trans nylon 6 *c*-axis repeat of 1.724 nm. Consequently, in the case of the λ-structure (Figure 3b), the strong underlying 002 meridional sublattice diffraction signal is sampled by the fifth order (005) of the 3.31 nm LSP. In the case of the sedimented mats from the nylon 8 chain-folded polymeric crystalline lamellae (Figure 3c), individual lamella (again ≈ a few nanometers thick) stack with random azimuthal rotation about the lamellar surface normal, and in situations like this, usually only one or two orders of the LSP are detected owing to the poor lamellar stacking.

(15) Sikorski, P.; Atkins, E. D. T. Manuscript in preparation.

(16) The value of γ^* was computed using the usual real to reciprocal angular relationship: $\cos\gamma^* = (\cos\alpha \cos\beta - \cos\gamma)/(\sin\alpha \sin\beta)$, and found to be 114.9°. For the monoclinic α-structure $\cos\gamma^* = -\cos\gamma$ (since $\alpha = \beta = 90°$). [If for any reason this is not the case (e.g. $\alpha \neq 90°$), the correct value of γ needs to be computed using the equation with $\beta = 90^o$ and $\gamma^* = 114.9°$.]

(17) Atkins, E. D. T.; Keller, A.; Sadler, D. M. *J. Polym. Sci., Polym Phys.* **1972**, *A2*, 863.

(18) When considering the intersheet energy as a function of Δc, there are two possible *a*-axis intersheet shear stacking modes for for the nylon 6 structure: $\pm\Delta a$. This feature has been discussed and investigated, for example in the β-sheet silk-like protein structures [e.g.: Geddes, A. J.; Parker, K. D.; Atkins, E. D. T.; Beighton, E. *J. Mol. Biol.* **1968**, *32*, 343. Krejchi, M. T.; Cooper, S. J.; Deguchi, Y.; Atkins, E. D. T.; Fournier, M. J.; Mason, T. P.; Tirrell, D. A. *Macromolecules* **1997**, *30*, 5012] and also more recently for nylon 6.[19] We find that in the case of nylon 6, the calculated energy profile minima are similar apart from an arbitrary change in origin for Δc.

(19) Leon, S.; Aleman, C.; Munoz-Guerra, S. *Macromolecules* **2000**, *33*, 5754.

(20) Because the hydrogen-bonded sheets have a center of symmetry with respect to *c*, the energy profiles reflect at $\Delta c = 0.862$ nm.

(21) The fact that the Δc values are the similar for both 5-amide nylon 6 and nylon 8 polymer at room temperature[13] would suggest that the origin of the *c*-axis shear emanates from interference between neighbouring intersheet amide units and that the difference between the alkane segments lengths for nylon 6 and nylon 8 are not particularly important.

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