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Temperature-Induced Changes in Lamellar Crystals of Monodisperse Nylon 6 and Nylon 6 6 Oligoamides

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ABSTRACT: The structural changes induced as a function of temperature in lamellar crystals of monodisperse oligoamides of nylon 6 and nylon 6 6 have been studied using differential scanning calorimetry, X-ray diffraction and electron diffraction. Three different types of solid-state transformations, differing in their mechanisms, rates and associated transformation temperatures, are evident: unfolding, intersheet shear and, for nylon 6 6 molecules only, a Brill transformation. Unfolding transformations in the chain-folded crystals can occur within 40 min in a temperature range ∼40 °C below the melting temperature, T_m, and can also be induced at lower temperatures over longer time periods. Changes in intersheet shear, from an alternating to a progressive scheme, can be induced at relatively low temperatures, e.g. ∼70 °C below T_m for the once-folded 9-amide nylon 6 oligomer lamellar crystals, if long time periods (∼days) are employed. Upon heating, all the nylon 6 6 oligomers exhibited Brill transformations prior to melting and they occur rapidly (<second) between 20 and 70 °C below T_m. The nylon 6 oligoamides do not undergo a Brill transformation, and all but the 3-amide nylon 6 oligomer, showed behavior analogous to the nylon 6 polymer. The 3-amide nylon 6 oligomer has a room temperature crystal structure that differs markedly from the nylon 6 polymer and exhibits a pattern of behavior closer to that of nylon 6 6. On the basis of these results, we offer structural interpretations for the nature of the intersheet shear, unfolding, and Brill transformation.

Introduction

We have recently undertaken structural and morphological studies on both folded and unfolded lamellar crystals of nylon 6 monodisperse oligoamides.[1−3] We now investigate the effect of temperature on these crystals and extend our studies to related nylon 6 6 oligoamides. In particular, we focus on the changes in the folding behavior (using low-angle X-ray diffraction) and the convergence of the two characteristic nylon interchain wide-angle diffraction spacings (associated with a Brill transformation).

The stable room temperature crystalline structures for nylons 6[4] and 6 6,[5] denoted as the α-phases, consist of all-trans chain conformations hydrogen-bonded into sheets (*ac*-plane); the intersheet stacking is controlled by van der Waals interactions. The detailed organization of the intrasheet structure and the manner in which the sheets stack to form a crystal differ between the two nylons. In nylon 6, adjacent intrasheet chains are antiparallel, the intrasheet hydrogen bonds shear in an alternating manner (a-sheets[6]), and the intersheet stacking has alternating shear parallel to the *ac*-plane; consequently, the chain segments are normal to the chain end surfaces (Figure 1a,c). Thus, each chain has two interchain near-neighbor amide units aligned in parallel and four aligned antiparallel. In contrast, the intrasheet hydrogen bonds shear progressively in nylon 6 6 (p-sheets[6]) and the intersheet shear in the *ac*-plane is also progressive; thus chain segments tilt relative to the surfaces created by the chain ends (Figure 1b,d). In this structure, all interchain near-neighbor amide units are aligned in parallel.

Nylon Chain-Folded Lamellae. In sedimented mats of chain-folded lamellar crystals, the lamellar stacking periodicity (LSP) represents the distance between lamellae and gives an upper limit for the lamellar thickness. It is known that the lamellar thickness of solution-grown lamellar crystals of nylon 6 6 polymers is dependent on the crystallization conditions,[7−9] i.e., solvents and temperature, and also on subsequent annealing; LSP values in the range 5−8 nm have been reported.[7−9] In melt-crystallized nylon 6 6, LSP values in the range 6−11 nm occur.[10] Chain-folded lamellar crystals of nylon 6 have not been studied so extensively, however; typical LSP values are ∼7 nm.[11]

In nylon 6 monodisperse oligoamides, changes in the LSP have also been reported.[12,13,1] In certain cases, discrete and relatively large increases in the LSP values indicate that a degree of *unfolding* has occurred in these lamellar structures, resulting in a greater proportion of straight chain to folded chain segments, and a concurrent increase in the melting temperature (T_m) of the lamellar crystals.[12,13,1]

Changes in the Characteristic Interchain Spacings: The Brill Transformation. The Brill transformation represents the attainment of a pseudohexagonal crystal structure and is a commonly found transformation that occurs in many nylons on heating. This transformation, first reported by Brill[14] in 1942 for nylon 6 6, is characterized by the convergence of the two characteristic interchain diffraction signals, at spacings of 0.44 nm (100) and 0.37 nm (010), to an intermediate value of 0.42 nm.

In this paper we present our results on changes in structure upon heating lamellar crystals of 3-amide, 5-amide, 9-amide, and 17-amide oligomers of nylon 6

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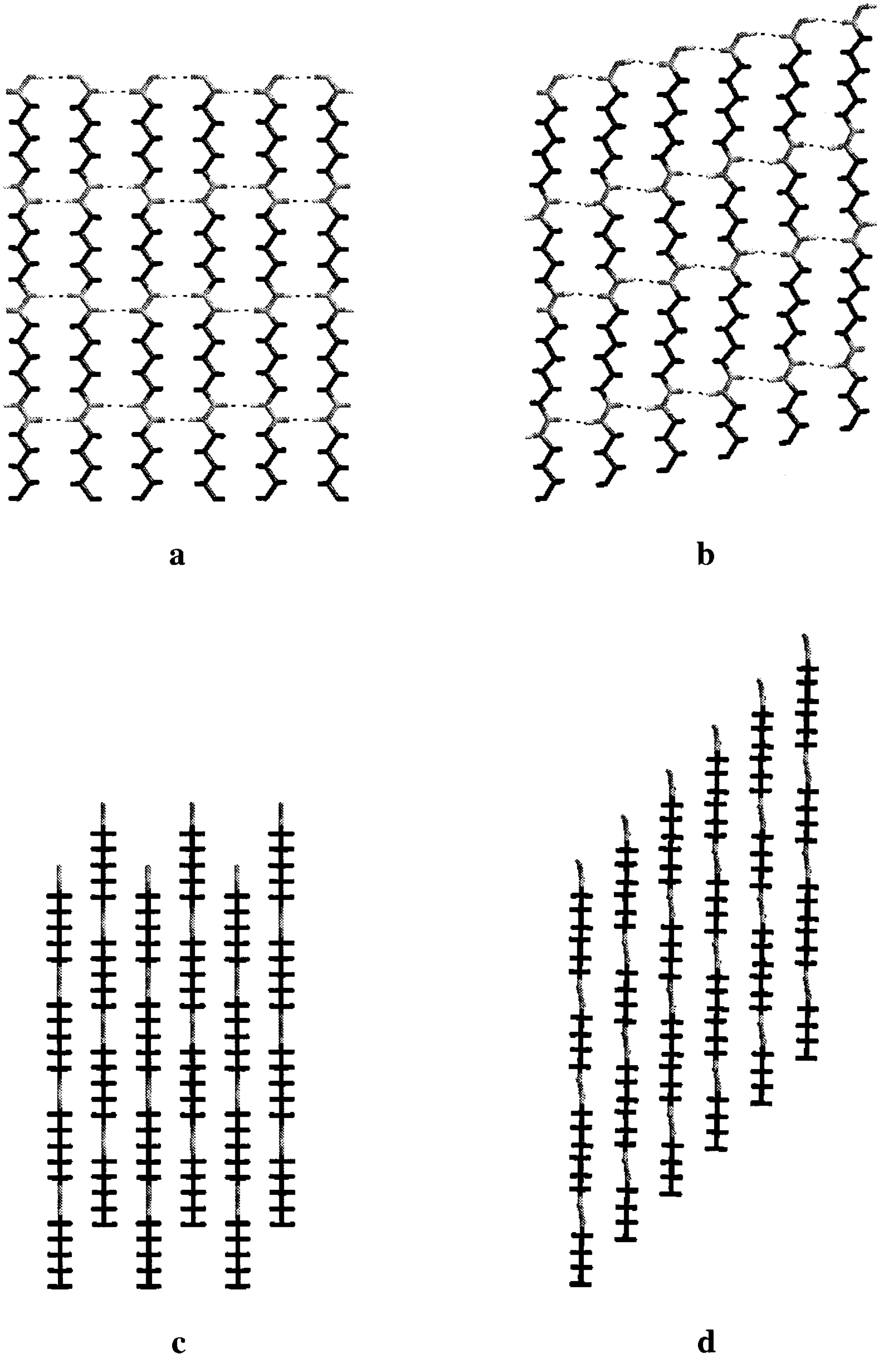

Figure 1. α-Phase room temperature structures for nylon 6 and nylon 6 6. Projections of the hydrogen-bonded sheets normal to the sheet surface are shown for (a) nylon 6 and (b) nylon 6 6. Views parallel to the hydrogen-bonded sheets shown in parts a and b are shown for (c) nylon 6 and (d) nylon 6 6. The methylene units are in black, the amide units are in gray, and the hydrogen bonds are indicated by dashed lines. Note in the nylon 6 structure that there is an alternating shear of the hydrogen bonds within the hydrogen-bonded sheets (a-sheets, part a) and also an alternating shear between successive sheets (part c). In contrast, in the nylon 6 6 structure, the hydrogen bonds shear progressively within the hydrogen-bonded sheets (p-sheets, part b), and there is also a progressive shear between the sheets (part d).

and 3-amide, 4-amide, 8-amide, 12-amide, and 16-amide oligomers of nylon 6 6, using differential scanning calorimetry and X-ray and electron diffraction. These monodisperse oligoamides have lengths in the range 3−15 nm, and the structures include unfolded-chain and chain-folded lamellar crystals. The nylon 6 6 oligoamides have room temperature structures similar to that of nylon 6 6 (Figure 1b,d). Similarly, the 5-amide,

Table 1. Crystallization Conditions and Crystal Structure at Room Temperature for the Nylon 6 and Nylon 6 6 Oligoamides and Nylon 6 and Nylon 6 6 Polymers

material	crystallization conditions	crystal structure at room temperature
3-amide nylon 6	Small quantities of dodecane were added to solutions of the oligoamide in excess chloroform. After filtration, the chloroform evaporation rate at room temperature governed the crystallization rate.	progressive chain shear with two hydrogen bond directions[2]
5-amide nylon 6	A solution of the oligoamide in DMF, saturated at ~80 °C, was heated to 100 °C to dissolve the oligoamide, and isothermally crystallized at 70 °C.	a-sheets with progressive intersheet shear[3]
5-amide nylon 6	A solution of the oligoamide in DMF, saturated at ~80 °C, was heated to 100 °C to dissolve the oligoamide, removed from the heat and allowed to cool to room temperature.	a-sheets with alternating intersheet shear[1,4]
9-amide nylon 6	Excess, filtered 1,4-dioxane was added to a filtered solution of the oligoamide in trifuoroethanol. The solution became turbid within a few minutes.	a-sheets with alternating intersheet shear[1,4]
17-amide nylon 6	Excess, filtered 1,4-dioxane was added to a filtered solution of the oligoamide in trifuoroethanol. The solution became turbid within a few minutes.	a-sheets with alternating intersheet shear[1,4]
nylon 6 polymer	A 0.05% (w/v) solution of nylon 6 in 1,4-butanediol was heated to 200 °C, seeded[32] at 190 °C, and isothermally crystallized at 115 °C.	a-sheets with alternating intersheet shear[4]
3-amide nylon 6 6	Small quantities of dodecane were added to solutions of the oligoamide in excess chloroform. After filtration, the chloroform evaporation rate at room temperature governed the crystallization rate.	p-sheets with progressive intersheet shear[2,5]
4-amide nylon 6 6	Small quantities of 1,4-dioxane were added to solutions of the oligoamide in excess trifluoroethanol. After filtration, the trifluoroethanol evaporation rate at room temperature governed the crystallization rate.	p-sheets with progressive intersheet shear[a]
8-amide nylon 6 6	Small quantities of 1,4-dioxane were added to solutions of the oligoamide in excess trifluoroethanol. After filtration, the trifluoroethanol evaporation rate at room temperature governed the crystallization rate.	p-sheets with progressive intersheet shear[b]
12-amide nylon 6 6	Small quantities of 1,4-dioxane were added to solutions of the oligoamide in excess trifluoroethanol. After filtration, the trifluoroethanol evaporation rate at room temperature governed the crystallization rate.	p-sheets with progressive intersheet shear[b]
16-amide nylon 6 6	Small quantities of 1,4-dioxane were added to solutions of the oligoamide in excess trifluoroethanol. After filtration, the trifluoroethanol evaporation rate at room temperature governed the crystallization rate.	p-sheets with progressive intersheet shear[b]
nylon 6 6 polymer	A 0.05% (w/v) solution of nylon 6 6 in 1,4-butanediol was heated to 200 °C, seeded[40] at 160 °C, and isothermally crystallized at 130 °C.	p-sheets with progressive intersheet shear[5]

[a] Based on oriented WAXS diffraction patterns from sedimented crystal mats. [b] Based on powder diffraction patterns at room temperature showing the typical 0.44 and 0.37 nm interchain spacings and an intrachain spacing of 0.64 nm typical of the projected interamide distance that occurs in progressively sheared p-sheet structures.

9-amide and 17-amide nylon 6 oligomers have room temperature structures analogous to that of nylon 6 (Figure 1a,c). However, we have also prepared 5-amide oligomer crystals which have a-sheets and progressive intersheet shear (Figure 1a,d),[3] while the 3-amide nylon 6 oligomer has a completely different room temperature structure based on hydrogen bonding in two directions between parallel (unidirectional) chains.[2] For all these crystals, we report on the changes in the LSP spacing as a function of temperature and on the structural interpretation and also on which oligoamides undergo a Brill transformation.

Experimental Section

Materials and Crystallization Conditions. The starting materials, in the form of purified powders, were kindly provided by Drs. G. Brooke and S. Mohammed, University of Durham, U.K., and the chemical synthesis and detailed characterization has been reported.[15−17] The oligoamide and polymer powder samples were obtained from precipitated crystals produced under the crystallization conditions outlined in Table 1.

Differential Scanning Calorimetry (DSC). T_ms of the oligoamide powder samples were measured using a Perkin-Elmer DSC 7 flushed with nitrogen. The heating rate was 10 °C/min.

X-ray Diffraction. X-ray diffraction data as a function of temperature were obtained using the synchrotron X-ray radiation source at the Daresbury Laboratory, U.K. Beam lines 8.2 and 16.1, which operate at fixed wavelengths of 0.154 and 0.140 nm, respectively, were used. Simultaneous SAXS (small-angle X-ray scattering) and WAXS (wide-angle X-ray scattering) measurements were obtained using an area detector and an image plate, respectively. A 2D detector was also used for collecting the wide-angle diffraction data from the shortest chain oligoamides, since the lamellae of these materials have LSP values outside the range of SAXS. Some data were collected using a point-collimated evacuated X-ray camera and a Siemens X-ray generator. All the powder samples were heated in a Linkham hot stage, and X-ray diffraction measurements were taken from room temperature up to the T_m of the samples. The temperature readings recorded were accurate to ±5 °C. Each WAXS pattern obtained using the image plate required ~15 min of processing time during the heating experiment. Consequently, the number of WAXS patterns taken with the image plate were necessarily limited at elevated temperatures close to T_m, to avoid degrading the samples.

Electron Diffraction (ED). Samples for transmission electron microscopy were prepared by depositing drops of the crystal suspension in nonsolvent (acetone for the oligoamide samples; 1,4-butanediol for nylon 6 6) onto carbon-coated grids and allowing the nonsolvent to evaporate. The samples were examined using a Phillips 400T TEM operating at 100 kV. Diffraction patterns were obtained as a function of temperature, between ambient temperature and T_m, by heating the crystals in a hot stage. Relative temperatures were accurate to within ±2 °C and absolute temperatures to within ±5 °C. Some crystals were decorated with platinum/palladium to calibrate the diffraction patterns.

Results and Discussion

DSC. DSC was used to give a general indication of the behavior of the nylon 6 and nylon 6 6 oligomers on heating. The traces for the unfolded 4-amide nylon 6 6 and for the (initially) once-folded 12-amide nylon 6 oligomers are shown in parts a and b of Figure 2,

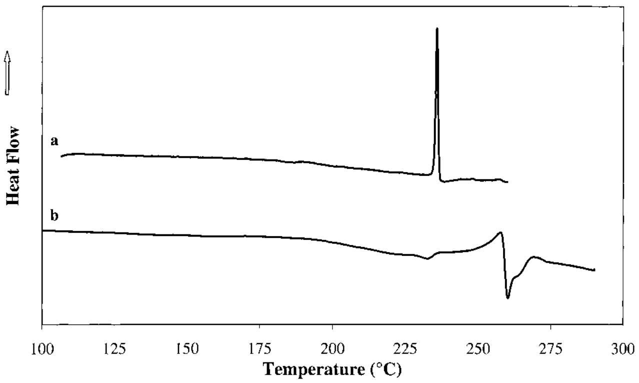

Figure 2. DSC traces on heating at 10 °C/min: (a) 4-amide nylon 6 6 lamellar crystals and (b) 12-amide nylon 6 lamellar crystals.

respectively. Figure 2a is typical of the DSC scans from all the initially unfolded nylon 6 and nylon 6 6 oligoamides that we examined on heating at 10 °C/min; it shows a single melting peak. The DSC traces from initially folded oligoamides are more complicated (e.g., see Figure 2b).

The T_ms of the nylon 6 and nylon 6 6 oligoamides, as determined by the temperature at which the final endothermic peak was seen in the DSC traces, are listed in the last columns of parts a and b of Table 2, respectively. Table 2a shows that the T_ms for the nylon 6 oligoamide series increase with the total number of amide units incorporated. The sheet stacking arrangement appears to have no discernible effect on the T_ms of the 5-amide nylon 6 oligomer (i.e., the alternatingly sheared a-sheet structure and the progressively sheared a-sheet structure both melt at 198 °C). In the nylon 6 6 oligoamide series, the T_ms increase to a maximum value for the 12-amide oligomer (Table 2b). Once the oligomers have chain lengths greater than the typical straight chain segments of the polymeric lamellar crystals, their melting temperatures are similar to those of the respective polymers. However, the T_ms of the 17-amide nylon 6 and 12-amide nylon 6 6 oligomers are greater than those of their respective polymers, and we believe that this is because the LSP values are larger, and therefore the crystals thicker, than those of the polymers.

The DSC traces of the oligoamides display a number of features in addition to the final endothermic melting peak. At lower temperatures, ~100−200 °C, the DSC traces of many of the oligoamides show broad, shallow endothermic peaks (see both parts of Figure 2); this feature, which is apparent on heating initially folded and (to a lesser extent) unfolded oligoamides, represents reorganization within the lamellae. In the folded lamellar crystals, endothermic and exothermic peaks are typically seen just prior to the final melting peak. This is illustrated in the DSC trace for the 12-amide nylon 6 6 crystals (Figure 2b). In general, we believe that these features are associated with the melting of the original (folded) lamellar structure, recrystallization in a lamellar structure with an increased LSP value and subsequent melting from this final form. However, at this stage we are not in a position to offer a direct correlation between these DSC features and specific structural transformations.

In the future, an extensive DSC program, including studies at different heating rates, annealing in the DSC, and crystallizing isothermally, should make it possible to assign these peaks with more certainty.

Changes in LSP: Unfolding. We observed a number of unfolding solid-state transformations (see parts a and b of Table 3) at elevated temperatures under our heating conditions, summarized as follows.

Nylon 6 Oligoamides (Table 3a). The 17-amide nylon 6 (chain length 15.0 nm) crystals exhibited an isothermal solid-state transformation from a twice-folded conformation (LSP = 5.4 nm[18]) to a once-folded conformation (LSP = 7.9 nm) after being kept at 175 °C for 10 min. On further heating to 185 °C, the LSP value increased further from 7.9 to 9.4 nm, suggesting that additional partial unfolding had occurred.

Nylon 6 6 Oligoamides (Table 3b). The 12-amide nylon 6 6 (chain length 10.7 nm) crystalline powders underwent a transformation from a once-folded conformation (LSP = 5.3 nm) to an unfolded conformation (LSP = 9.1 nm) within a 40 min interval in which the sample was heated in steps of 10 °C from 220 to 260 °C. During this time, the original LSP diffraction signal became weaker and diffuse and then disappeared at a temperature of 230 °C; however, the WAXS pattern did *not* change. The LSP diffraction signal (together with

Table 2. Changes in the Characteristic Interchain Diffraction Spacings

(a) Nylon 6 Oligomides and Nylon 6 Polymer[a]

material	structure at room temperature	interchain spacing at room temperature	interchain spacings just prior to melting	T_m (°C)
3-amide nylon 6	progressive chain shear with two hydrogen bond directions[2]	0.44, 0.37	0.42, 0.41	157
5-amide nylon 6	a-sheets with progressive intersheet shear[3]	0.44, 0.37	0.43, 0.40	198
5-amide nylon 6	a-sheets with alternating intersheet shear[1,4]	0.44, 0.37	0.42, 0.39	198
9-amide nylon 6	a-sheets with alternating intersheet shear[1,4]	0.44, 0.37	0.43, 0.39	209
17-amide nylon 6	a-sheets with alternating intersheet shear[1,4]	0.44, 0.37	0.42, 0.40	222
nylon 6 polymer	a-sheets with alternating intersheet shear[4]	0.44, 0.37	0.43, 0.40	218

(b) Nylon 6 6 Oligoamides and Nylon 6 6 Polymer[b]

material	structure at room temperature	interchain spacings at room temperature	T_B (°C) ± 5 °C	T_m (°C)
3-amide nylon 6 6	p-sheets with progressive intersheet shear[2]	0.44, 0.37	155	177
4-amide nylon 6 6	p-sheets with progressive intersheet shear	0.44, 0.37	205	236
8-amide nylon 6 6	p-sheets with progressive intersheet shear	0.44, 0.37	210	268
12-amide nylon 6 6	p-sheets with progressive intersheet shear	0.44, 0.37	205	276
16-amide nylon 6 6	p-sheets with progressive intersheet shear	0.44, 0.37	190	260
nylon 6 6 polymer	p-sheets with progressive intersheet shear[5]	0.44, 0.37	210	262

[a] These materials do *not* undergo a Brill transformation prior to melting. [b] All these materials undergo a Brill transformation prior to melting. The Brill spacing in each case is 0.42 nm.

Table 3. Changes in the LSP Spacing Upon Heating

(a) Nylon 6 Oligoamides and Nylon 6 Polymer

material	chain length (nm)	LSP and folding status at room temperature	LSP and folding status at elevated temperatures	time at $T \geq T_m - 40$ °C (min)	comments
3-amide nylon 6	3.0	LSP = 2.2 nm; unfolded	LSP = 2.5 nm at 155 °C; unfolded for all $T \leq T_m$	∼20	gradual change in intersheet shear[c]
5-amide nylon 6[a]	4.6	LSP = 3.4 nm; unfolded	LSP = 3.7 nm at 195 °C; unfolded for all $T \leq T_m$	∼30	gradual change in intersheet shear[d]
5-amide nylon 6[b]	4.6	LSP = 4.8 nm, unfolded	not measured; presume unfolded for all $T \leq T_m$	∼10	
9-amide nylon 6	8.0	LSP = 4.8 nm; once-folded, 4 amides in straight stem	After annealing at 140 °C for 24 h, LSP = 4.6 nm; ∼5 amides in straight stem	24 h at 140 °C, LSP at higher *T* not measured	transformation in intersheet stacking arrangement from an alternating to progressive scheme occurred during annealing
17-amide nylon 6	15.0	LSP = 5.4 nm; twice-folded, 5 amides in straight stem	LSP = 7.9 nm at 175 °C; once-folded, 8 amides in straight stem LSP = 9.4 nm at 185 °C; once folded, ∼10 amides in straight stem	∼15 (∼30 min for $T \geq T_m - 50$ °C)	isothermal unfolding to a once-folded conformation at 175 °C with further partial unfolding at 185 °C
nylon 6 polymer	>150	LSP = 5.8 nm; folded, ∼6 amides in straight stem	LSP = 6.2 nm at 195 °C; folded, ∼7 amides in straight stem	∼80	some degree of partial unfolding occurred

Nylon 6 6 Oligoamides and Nylon 6 6 Polymer

material	chain length (nm)	LSP and folding status at room temperature	LSP and folding status at elevated temps	time at $T \geq T_m - 40$ °C (min)	comments
3-amide nylon 6 6	3.0	LSP = 2.2 nm; unfolded	LSP = 2.4 nm at 175 °C; unfolded for all $T \leq T_m$	∼20	gradual change in intersheet shear[e]
4-amide nylon 6 6	3.8	LSP = 2.9 nm; unfolded	LSP = 3.0 nm at 220 °C; unfolded for all $T \leq T_m$	∼40	gradual change in intersheet shear[e]
8-amide nylon 6 6	7.2	uncertainty regarding the LSP signal	LSP = 5.4 nm at 250 °C; unfolded	∼20	uncertainty regarding the transformation at 250 °C (see text)
12-amide nylon 6 6	10.7	LSP = 5.3 nm; once-folded	LSP signal disappears at 230 °C LSP = 9.1 nm at 250 °C; unfolded	∼60 (∼75 min for $T \geq T_m - 50$ °C)	folded to unfolded chain transformation at 250 °C gradual change in intersheet shear[f]
16-amide nylon 6 6	14.1	LSP = 5.2 nm; once-folded, 8 amides in straight stem	LSP signal became weak and diffuse at 220 °C and disappeared at 230 °C due to sample degradation	∼65	sample degraded slightly at higher *T* and the LSP signal disappeared (the WAXS pattern remained, though)
nylon 6 6 polymer	>150	LSP = 5.4 nm; folded, ∼8 amides in straight stem	LSP = 5.7 nm at 205 °C; folded, ∼8 amides in straight stem	∼10	gradual change in intersheet shear[f]

[a] Structure with a-sheets and progressive intersheet shear (Figure 1a,d). [b] Structure with a-sheets and alternating intersheet shear, i.e., analogous to the nylon 6 polymer structure (Figure 1a,c). [c] The intersheet shear changed from ∼42° at room temperature to ∼32° prior to melting, based on the observed decrease in LSP spacing and estimated reductions in the *c*-value of 2%[21] prior to melting. [d] The intersheet shearchanged from ∼42° at room temperature to ∼35° prior to melting, based on the observed decrease in LSP spacing and estimated reductions in the *c*-value of 2%[21] prior to melting. [e] The intersheet shear changed from ∼42° at room temperature to ∼34° prior to melting, based on the observed decrease in LSP spacing and estimated reductions in the *c*-value of 4.0%[21] prior to melting. [f] The intersheet shear changed from ∼42° at room temperature to ∼34° prior to melting, based on the increase in the spacing of the room temperature 0.64 nm intrachain (002) diffraction signal seen in the WAXS patterns and estimated reductions in the *c*-value of 4%[21] prior to melting.

its second order) reappeared at the increased spacing of 9.1 nm at 250 °C (see Figure 3 and Table 3b).

The 8-amide nylon 6 6 (chain length 7.2 nm) crystalline powders at room temperature gave the usual nylon 6 6 polymer wide-angle X-ray diffraction pattern, but no LSP diffraction signal was observed. (The ranges available in the experiment using the synchrotron source were 10 nm to 3 nm [low-angle] and 2 nm to 0.1 nm [wide-angle]; thus we had a blind spot between 2 and 3 nm.) As the sample was incrementally heated, a sharp LSP diffraction ring appeared at 250 °C with a of spacing 5.4 nm[18] (Table 3), and some of the higher orders were also observed in the wide-angle X-ray pattern being simultaneously recorded. These diffraction results suggests good stacking of lamellae with each lamella composed of tilted unfolded chains.[18] This structure remained on cooling to room temperature. On the basis of these results we can only speculate on our inability to observe a LSP diffraction signal(s) from the room temperature sample prior to heat treatment. One possibility is that at room temperature the 8-amide nylon 6 6 molecules have a once-folded conformation and the LSP diffraction signal, expected to be around 2.5 nm, fell in the experimental blind spot. (The LSP from oligoamide crystals containing chain-folded lamellae usually only show the first order[1]). The relatively

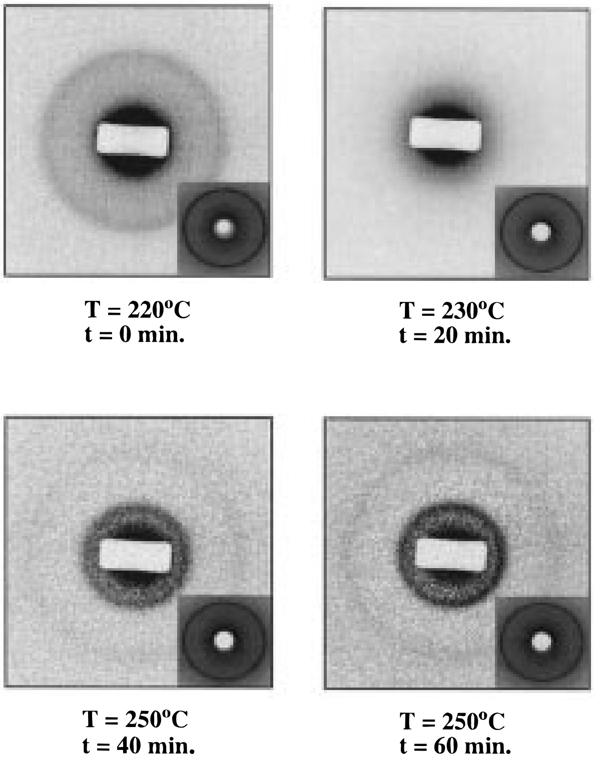

Figure 3. SAXS patterns of the 12-amide nylon 6 6 oligomer crystals at elevated temperatures, with the WAXS patterns taken at the same temperature and time shown as insets. The LSP signal at 5.3 nm at 220 °C disappears at 230 °C and then reappears (together with its second order) at the increased LSP value of 9.1 nm at 250 °C. Note that although the LSP signal disappears at 230 °C, the WAXS signal remains.

sudden appearance of the 5.4 nm LSP lattice at 250 °C suggests something rather dramatic is happening, such as chains unfolding, as found for the 12-amide nylon 6 6 lamellar crystals at a similar temperature. A second possibility is that at room temperature the molecules are unfolded but in poorly stacked lamellae; indeed, so poor that a LSP diffraction signal is not generated. On heating, a LSP lattice is created by annealing. However, if this were the case, it would be expected to occur at a lower temperature and to be a more gradual change. Thus, further studies on the 8-amide nylon 6 6 oligomer are needed to clarify this issue.

Changes in Lamellar Structure: Chain Shear Transformations. Slight changes in the intersheet shear, represented by the crystallographic angle, α, occur upon heating nylons with progressive intersheet shear;[19] e.g., a gradual, continuous change in intersheet shear occurs in nylon 6 6 from 100 °C ($\alpha = 48.5°$) to melting ($\alpha \sim 56°$).[20−22] These subtle changes in the magnitude of the intersheet shear arise as a consequence of the increased librational motion of the chain segments at elevated temperatures (as does the observed decrease in the unit cell *c*-value) and represent only small local alterations.

In contrast, a dramatic change in the intersheet stacking arrangement was observed for the once-folded 9-amide nylon 6 oligomer when it was annealed at 140 °C, for 24 h and then cooled to room temperature. The lamellar crystals transformed from a room-temperature structure with an alternating intersheet shear to a progressive intersheet shear, as indicated by the 0.37 nm intersheet diffraction signal changing from an equatorial to an off-equatorial position (Figure 4, Table 3b). Thus, a folded structure analogous to the unfolded 5-amide nylon 6 structure with a-sheets stacked progressively was attained, i.e., a structure combining the features of parts a and d of Figure 1. During this process, the LSP value changed from 4.9 nm, a spacing commensurate with four amide units in the *c*-direction parallel to the lamellar normal, to 4.3 nm, a spacing commensurate with five amide units in the *c*-direction in this progressively sheared structure with the chain segments inclined (~40°) to the lamellar normal.[18]

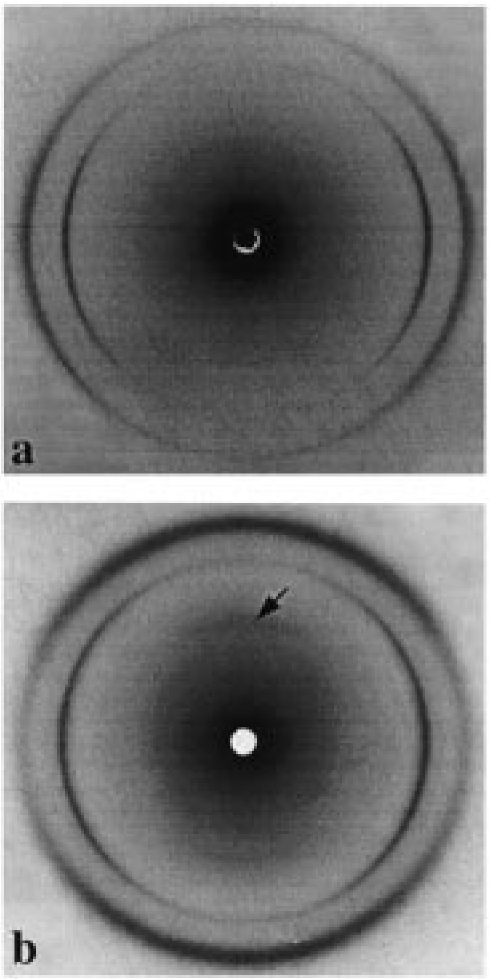

Figure 4. Wide-angle X-ray diffraction patterns of oriented sedimented crystal mats of the 9-amide nylon 6 oligomer crystals at room temperature of (a) the unannealed sample and (b) sample annealed at 140 °C for 24 h. Note that the outer 0.37 nm intersheet signal has moved from an equatorial position in part a to an off-equatorial position in part b. In addition, the inner 0.44 nm signal has moved ~10° off the equator in part b, and the 002 meridional diffraction signal at a spacing of 0.64 nm is observed (arrowed).

Changes in Lamellar Structure: the Brill Transformation. Changes in the two characteristic interchain spacings of the nylon 6 and nylon 6 6 oligoamides are detailed in parts a and b of Table 2, respectively. There was good agreement between the ED and X-ray diffraction results.

Nylon 6 and Its Oligoamides: Table 2a. Lamellar crystals of the nylon 6 polymer do not undergo a Brill transformation prior to melting (this is similar to the behavior of the other low even nylons, nylons 4[23] and 8[24]), although the two characteristic interchain diffrac-

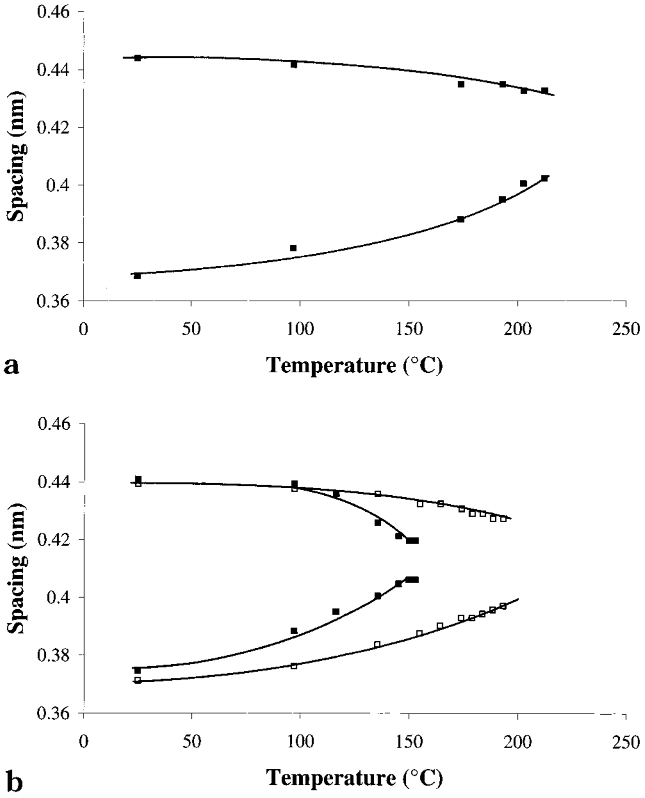

Figure 5. Variation in the spacing of the two characteristic interchain signals with temperature for (a) nylon 6 polymer, and (b) 3-amide nylon 6 oligomer (filled squares) and the 5-amide nylon 6 oligomer with the room temperature structure consisting of a-sheets stacked with progressive shear (unfilled squares). All the nylon 6 oligomers, other than the 3-amide oligomer, show behavior similar to the nylon 6 polymer.

tion signals do move together as the crystals are heated, as shown in Figure 5a.

None of our nylon 6 oligoamides undergo a Brill transformation either (Table 2a); typical traces are shown in Figure 5b. It is of particular interest that the two crystal forms of the 5-amide nylon 6 oligomer, which differed in their sheet stacking arrangements (i.e. one alternating, the other progressive), displayed similar behavior. Clearly, the stacking mode of the hydrogen-bonded sheets has little effect on the attainment, or otherwise, of the Brill pseudohexagonal structure. The 3-amide nylon 6 oligomer behaved somewhat differently from the nylon 6 polymer and its other oligoamides (compare parts a and b of Figure 5). The 3-amide nylon 6 oligomer comes closest to undergoing a Brill transformation; the two principal interchain spacings almost converge, with values of 0.42 and 0.41 nm, at 150 °C just prior to melting. Interestingly, the 3-amide nylon 6 oligomer is the only nylon 6 oligomer that has a markedly different room-temperature structure from that of the nylon 6 polymer; its room-temperature crystal phase is based on hydrogen bonding in two directions between parallel chains.[2] In this structure, in contrast to the nylon 6 polymer but similar to the nylon 6 6 polymer, the chains are inclined at a substantial angle (~40°) to the lamellar normal.[2]

Nylon 6 6 and Its Oligoamides: Table 2b. All the nylon 6 6 oligoamide crystals studied exhibited Brill transformations prior to melting (Table 2b). The 3-amide nylon 6 6 oligomer had a Brill temperature, T_B, of 155 °C, ~20 °C below the T_m. All the other nylon 6 6 oligoamides studied had T_Bs in the range of 190−210 °C, showing behavior entirely analogous to that of the nylon 6 6 polymer, for which the T_Bs for solution-grown lamellar crystals have been recorded at ~220 °C.[25] The Brill graphs for the 3-amide and 12-amide nylon 6 6 oligomers are shown in Figure 6. The behavior of the nylon 6 6 polymer is the same as that of the 12-amide nylon 6 6 oligomer.

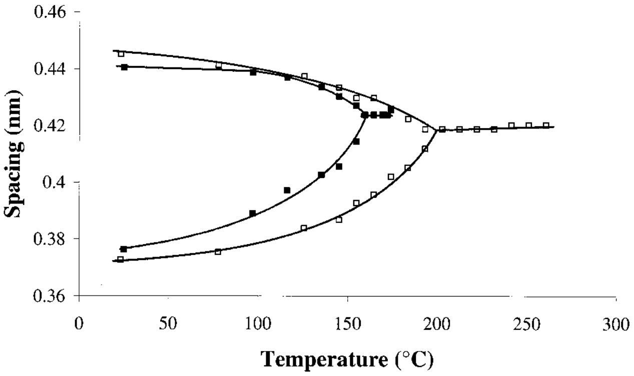

Figure 6. Variation in the spacing of the two characteristic interchain signals with temperature for 3-amide nylon 6 6 oligomer (filled squares) and 12-amide nylon 6 6 oligomer (unfilled squares). The behavior of the other nylon 6 6 oligomers is the same as that of the 12-amide oligomer.

General Discussion

The following solid-state transformations can occur as a function of temperature in the oligoamide lamellar crystals: unfolding transformations, intersheet shear transformations, and Brill transformations. These transformations differ in both their rates and associated transformation temperatures.

Unfolding Transformations. The discontinuous, discrete increases in the LSP of oligoamide lamellar crystals observed in this study suggest that unfolding processes can occur to a substantial degree in the solid state. It appears that unfolding can proceed at relatively low temperatures, ~70 °C below T_m, over long time periods; e.g., a partial unfolding occurs on annealing the 9-amide nylon 6 crystals for 24 h at 140 °C and can certainly occur within 40 min. at temperatures ~40 °C below T_m. Prior to the discrete increase in the LSP value, the original LSP diffraction signal becomes weak and diffuse and finally disappears; however, the WAXS pattern is maintained throughout this process (see Figure 3). This illustrates that the transformation propagates throughout the lamellae and does not involve full-scale disruption of the whole interlamellar structure.

The unfolding mechanism requires the cooperative breaking and subsequent re-forming of hydrogen bonds along the whole length of the straight stem. For example, in once-folded 12-amide nylon 6 6 lamellar crystals, the unfolding transformation implies an activation energy associated with the cooperative breaking of at least six hydrogen bonds along the length of the straight stem. Similarly, in the once-folded 9-amide nylon 6 and twice-folded 17-amide nylon 6 lamellar crystals, at least four hydrogen bonds would need to be broken cooperatively.

Intersheet Shear Transformations. The change in the intersheet shear arrangement, from alternating to progressive, in the 9-amide nylon 6 oligomer occurred after heating the lamellar crystals at the relatively low temperature of 140 °C for 24 h. No evidence of such a dramatic change in the intersheet shear was observed for the 5-amide and 17-amide nylon 6 oligomers, or indeed the nylon 6 polymer, on heating these lamellar crystals more rapidly to higher temperatures up to melting. The intersheet shear transformation appears to be representative of a process with a low activation energy that requires considerable cooperativity of motion. Due to the directionally nonspecific van der Waals intersheet forces, slippage of the sheets can occur easily; however, the extensive intersheet reorganization is statistically prohibitive on small time scales. The transformation could be likened to smectic liquid-crystalline behavior involving whole sheet slippage.

Brill Transformation. *Nylon 6 and Its Oligoamides.* For nylon 6 and its 5-, 9-, and 17-amide oligomers, our results indicate that the a-sheet architecture hinders the formation of the Brill pseudohexagonal structure. The hydrogen-bonding scheme in a-sheets occurs between antiparallel amide units; consequently, in these structures, a particular amide unit will have two interchain near-neighbor amide units aligned in parallel and four interchain near-neighbor amide units aligned antiparallel. In contrast, the hydrogen bonding in p-sheets occurs between unidirectional amides; hence, a particular amide unit will have all its interchain near-neighbor amide units aligned in parallel. Of all the nylon 6 oligomers studied, the 3-amide nylon 6 oligomer comes closest to a Brill transformation. The crystal structure of this oligoamide is based on hydrogen bonding in two directions and all the amides are parallel, indicating that either the unidirectionality of hydrogen-bonded amides and/or the presence of hydrogen bonding in more than one direction, aids the formation of the Brill structure. We believe that the Brill transformation represents the attainment of a structure with hydrogen bonds in three trigonal directions; the population in each direction will be determined by the strength of the hydrogen bonds formed in that direction. If three directions of hydrogen bonds do exist in the Brill pseudohexagonal structure, then we might expect that the attainment of the Brill structure would be easier if all the hydrogen bonds were formed between unidirectional (parallel) amide units, since all the amide units will have the same criteria for optimum hydrogen bonding.

Nylon 6 6 and Its Oligoamides. The similarity of the Brill behavior of the 4-, 8-, 12-, and 16-amide nylon 6 6 oligomers and the nylon 6 6 polymer, despite a substantial relative change in chain length within the series, suggests that the length of a particular nylon will have little effect on T_B. Furthermore, T_B is not dependent upon T_m, except for the 3-amide nylon 6 6 oligomer crystals, for which T_m is 177 °C, substantially lower than the other members of the series (Table 2b). The Brill transformation occurs rapidly and represents the attainment of additional locally accessible conformational states. The additional conformations can only be attained at higher temperatures, but since the attainment involves only small-scale motion of the constituent atoms, it is likely to occur on the time scale of molecular librations ($\sim 10^{-15}$s). The exact time will be dependent on the cooperativity of the motion required.

Brill Transformation Models. Currently, there are various models proposed for the nylon 6 6 structure above T_B. Brill[14] proposed that the convergence and coalescence of the two principal interchain diffraction signals, characteristic of the nylon 6 6 room temperature structure[5] (see also Introduction), to a single diffraction signal at 4.2 nm spacing at T_B (~160 °C for fibers), well below T_m at 265 °C, was a consequence of the interchain hydrogen bonds reorganizing into a hexagonal arrangement. This model would demand a substantial proportion of the intersheet hydrogen bonds breaking and re-forming as intersheet hydrogen bonds; indeed, the original hydrogen-bonded sheet structure stacking via van der Waals interactions would lose its identity. However a number of authors, for example,[20,21,26,27] based on birefringence,[26] X-ray structural studies,[21,27] and NMR,[20] have argued that the hydrogen bonds remain solely within the sheets for another 100 °C or so above T_B, all the way up to T_m. In the case of the NMR experiments of Hirschinger et al.,[20] it was argued that the Brill transformation represents the onset of large amplitude librational motion of the alkane segments and that the hydrogen bonds *do not* break.

As we see it, any three-dimensional crystalline model structure for nylon 6 6 with *no* intersheet hydrogen bonds, i.e., with only van der Waals interactions to sustain it in one of the principal crystal directions, has an inherent weakness. When the room temperature nylon 6 6 structure is heated to T_B, the intersheet distance (controlled by van der Waals interactions) has already increased by 13.5% (from 0.37 to 0.42 nm), and therefore, the intersheet interactions are weakened as a consequence. Thus, the question arises: above T_B what sustains this weak intersheet bonding, at the particular value of 0.42 nm,[28] and prevents the sheets moving further apart for another 100 °C or so to T_m? Model structures with hydrogen bonds solely within the sheets need to address and offer an explanation for this problem for the structure of nylon 6 6 above T_B.

Undoubtedly the alkane segments do undergo large amplitude librational motion above T_B, and we consider that this motion will exert a torsional force on the adjacent amide units, resulting in the intermittent breaking of the intersheet hydrogen bonds. A cooperative rearrangement of the hydrogen bonds into one or more different directions may then occur provided sufficiently strong hydrogen bonds can be formed in these directions.[29,30] For a fully hexagonal structure (e.g. the nylon 6 9 high-temperature phase[31]), this condition is obviously met. However, even for the nylon 6 6 pseudohexagonal structure, the substantial freedom of the alkane segments should allow hydrogen bonds to form in other directions. The population of hydrogen bonds will not be equal in the three trigonal directions in the nylon 6 6 high temperature ($T_B < T < T_m$) structure. Hence, our model is not inconsistent with either the birefringence[26] or the X-ray structural studies.[21,27]

The time scale on which this transformation would occur will be determined by the extent of the cooperativity of motion required to form stable hydrogen bonds in the new directions. Without knowing the exact time scale, it is difficult to ascertain whether the NMR experiments of Hirschinger et al.[20] could determine whether a degree of hydrogen bond rearrangement was occurring.

Conclusions

The monodisperse oligoamides studied can undergo solid-state transformations involving change in intersheet shear, unfolding, and chain packing (the Brill transformation). The intersheet shear and unfolding transformations require *extensive*, cooperative atomic motion *along* the chain direction and involve the breaking of mainly van der Waals forces for the intersheet shear transformation and both van der Waals and hydrogen bonds for the unfolding transformation. In contrast, the Brill transformation only involves cooperative *local* atomic motion *orthogonal* to the chain axis. Consequently, the Brill process occurs on a quicker time scale than the former two processes. The activation energies for both the intersheet shear and unfolding transformations appear to be less than that for the Brill transformation, as these processes can occur at lower temperatures (given sufficient time) than those associated with the Brill transformation. Since unfolding transformations can proceed at temperatures well below T_m and must involve the cooperative breaking of hydrogen bonds along the chain direction, this suggests that cooperative breaking of hydrogen bonds along the a-direction can also occur below T_m, and may form the basis of the Brill transformation.

The oligomers of nylon 6 that have an alternating hydrogen-bonded sheet structure do not undergo a Brill transformation before melting. The sheet stacking arrangement has little effect on the attainment, or otherwise, of the Brill pseudohexagonal structure, since the variation of the two characteristic interchain diffraction signals upon heating was independent of whether the 5-amide nylon 6 lamellar crystals had either an alternating or progressive intersheet shear. The 3-amide nylon 6 oligomer shows a different behavior on heating from that of the nylon 6 polymer and indeed of all the other nylon 6 oligomers. Although the 3-amide nylon 6 does not undergo a Brill transformation before melting, the two prominent interchain diffraction signals are closer together prior to melting. The 3-amide nylon 6 oligomer has a crystal structure based on hydrogen bonding in two directions between parallel chains, suggesting that either of these factors may increase the likelihood of a particular oligoamide, or nylon, undergoing a Brill transformation.

All the nylon 6 6 oligomers undergo Brill transformations prior to melting. T_B is independent of both T_m and the length of the oligoamide chain, once the oligoamide contains more than three amide units. This suggests that neither the molecular weight of the nylon 6 6 sample nor its T_m has a significant effect on the Brill transformation. The ability of the nylon 6 6 polymer to undergo a Brill transformation, when the same transformation is not seen in the nylon 6 polymer, which has the same linear density of hydrogen bonds, appears linked to either the presence of all parallel interchain near-neighbor amides, or it is intrinsic to the chemical sequence of nylon 6 6 (and other even−even nylons).

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(19) A similar change in the magnitude of the intersheet shear may also occur on heating crystals with an alternating intersheet shear, such as nylon 6, although in this case, any change in intersheet shear will not be exemplified by a change in the unit cell parameters, or by an obvious change in the WAXS patterns. In nylon 6 polymer, the magnitude of the alternating intersheet shear may be determined from the relative intensity of the 002 and 012 diffraction signals.
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