

A neutron diffraction study of the fold surface in solution-grown 6,6-nylon crystals

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6,6-Nylon has been polymerized using d_8 -adipic acid. For a regular fold surface, the interior of the d_8 -6,6-nylon crystals then involves a regular alternation of regions with high and low scattering length density. Neutron diffraction data obtained at wavelengths of 4.7 and 2.35 Å* show slight shifts in the 001 peak position with a change in swelling agent from butane, 1,4-diol to the d_8 -analogue. On the basis of calculated diffraction intensities these shifts are shown to be consistent with a majority of acid-type folds in the single crystals, a feature consistent with earlier X-ray data. The proportion of acid-type folds is estimated to be 0.58.

(Keywords: nylon; crystals; neutron diffraction; chain folding)

INTRODUCTION

In chain-folded crystalline polymers, small angle X-ray scattering generally provides information on the periodicity of lamellar stacking. This in turn provides information, albeit indirect, on the nature of the fold surface of the lamellae. The unusual structure of 6,6-nylon single crystals leads to specific features in the X-ray diffraction patterns which are directly related to the nature and regularity of crystal stems (i.e. individual traverses of the crystal) themselves.

The thickness of 6,6-nylon single crystals is generally relatively small¹. In combination with the large chemical repeat unit, this results in a small number of repeat units per crystal traverse. This fact is responsible for unusual X-ray diffraction effects previously observed^{2,3}: combined small and wide angle X-ray measurements showed weak meridional reflections between the low angle and 001 arcs, and between the 001 and 002 reflections. The number (n) of these latter subsidiary maxima was shown to be related to the number of crystallographic repeat units in the lattice ($n + 2$). In general, polymer single crystals are characterized by large values of n and such subsidiary maxima are, therefore, not observed.

In this work, we consider crystallization of 6,6-nylon from dilute solution in butane 1,4-diol at 120°C. This results in two subsidiary maxima ($n = 2$), corresponding to four repeat units within the lamellae. Measurement of the relative intensities of Bragg reflections and subsidiary maxima previously led to the conclusion that most folds, in crystals obtained under these conditions, incorporate the acid component of the chemical repeat unit³. Results from infrared spectroscopy⁴ conversely suggested some irregularity in folding for 6,6-nylon single crystals, with a regular fold band being assigned to an amine fold.

More recently, the annealing of crystal suspensions above their original crystallization temperatures (T_c) has produced long periods (l) larger than previously reported⁵. These observations correspond to an upswing in the well established plateau region of l as a function of T_c . For the largest values of l , three subsidiary maxima were observed between the 001 and 002 X-ray reflections, the intensities again providing support for an acid fold model.

The presence of subsidiary maxima in itself is indicative of regularity of the fold surface, while their intensity provides evidence for the type of fold involved. To clarify the results obtained from previous X-ray diffraction experiments, complementary neutron diffraction experiments are described here. In the X-ray diffraction case, 00 l intensities are primarily determined by the arrangement of planes of oxygen atoms within lamellae. To obtain the required contrast in the neutron scattering experiment, it was necessary to label part of the polymer chain isotopically. d_8 -6,6-nylon was synthesized using fully deuterated adipic acid, providing a polymer with fully deuterated acid blocks. In the neutron diffraction experiment, the alternate layers, within the lamellae, of deuterated acid and hydrogenous amine blocks, with their differences in scattering length density, are responsible for the meridional intensity distribution.

By comparison with the meridional Bragg reflections, the subsidiary maxima in neutron diffraction were found to be too weak for quantitative use. Nevertheless, a secondary effect was encountered: to minimize interference effects from lamellar stacking, the single crystal mats were swollen with butane 1,4-diol. A change in the position of the 001 Bragg peak was found to accompany a change in the isotopic labelling of the swelling agent. The magnitude and sign of the change in position are related to the arrangement of acid and amine blocks within the crystal.

* 1 Å = 10⁻¹ nm

Measurements are reported here from two neutron spectrometers, using different wavelengths, and the results are discussed in terms of possible models of lamellar structure in 6,6-nylon.

CHAIN CONFORMATION WITHIN LAMELLAE

The observation of two subsidiary X-ray reflections between the 001 and 002 peaks in solution crystallized 6,6-nylon and the correspondence between a multiple of the crystallographic repeat distance and the size of the four repeat unit traverse have led to the conclusion that the crystal stems terminate in a regular and compact fold³. It was shown that a structure involving an alternation of acid and amine folds was not compatible with the small fold layer thickness. The structure is, therefore, likely to involve lamellae with uniformly one chemical type of fold, although it would be possible to have different lamellae with different fold types.

As mentioned above, the 00*l* intensity distribution in the X-ray diffraction experiment primarily arises from the electron-dense layers of oxygen atoms within the lamellae. For d₈-6,6-nylon with chemical repeat unit



the coherent scattering lengths for the individual chemical groups are listed in Table 1. These figures give rise to a regular alternation between high and low values of

Table 1 Coherent neutron scattering lengths for chemical groups present in d₈-6,6-nylon

Chemical group	10 ¹² Σ b (cm) ^a
CH ₂	-0.087
CD ₂	1.995
CO	1.238
NH	0.566

^aSummed over elements present

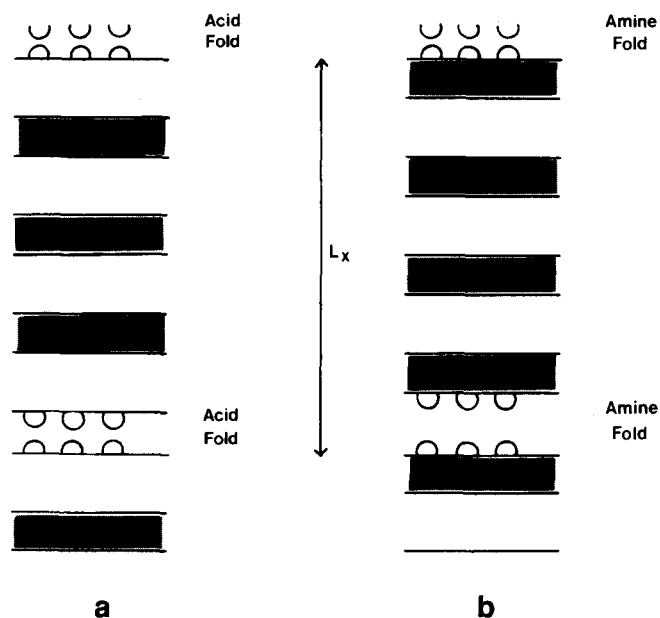


Figure 1 Schematic cross section of 6,6-nylon lamellae showing (a) the acid section of the repeat unit forming the fold and (b) the amine section forming the fold. The acid segments within the lamellae are shown shaded. L_x is the X-ray long spacing

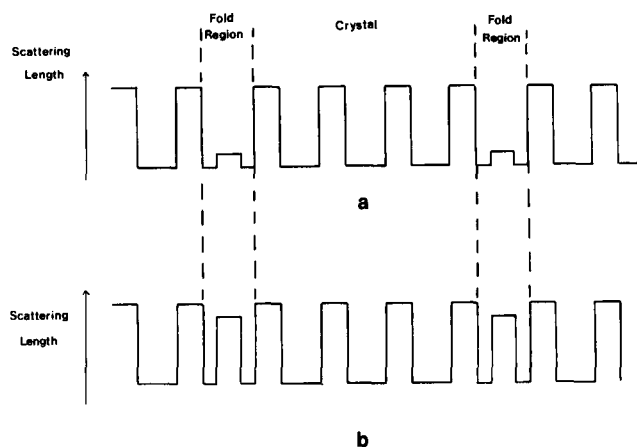


Figure 2 Schematic representations of the variation in scattering length on traversing d₈-6,6-nylon crystals, assuming an amine fold. (a) Shows the situation for hydrogenous swelling agent and (b) is for deuterated swelling agent. The label 'fold region' includes both the extended folds and interlamellar solvent. Plots are not drawn to scale

scattering length along the polymer chain, with the acid segment showing higher values. If the fold surface of a lamella contains only folds of one type, then the lamella may be considered as a composite, with layers of alternately high and low scattering length density. Figure 1 illustrates schematically the crystal composition for chain conformations with regular acid folds and with regular amine folds. The figure represents crystals with four repeat units within the crystal traverse.

As in previous X-ray measurements, 6,6-nylon mats were swollen with butane 1,4-diol to minimize interference effects due to lamellar stacking. The use of either hydrogenous or deuterated swelling agent introduces a further change in scattering contrast: this is illustrated in Figure 2, where the variation in scattering length through the lamella (including the swollen fold regions) is shown for (arbitrarily) the amine fold model. The folds themselves are extended by the solvent and the crystals separated, as indicated by the increase in X-ray long spacing³.

It will be necessary to consider four possible arrangements to model the behaviour of the polymer in both hydrogenous and deuterated swelling agent: diffraction will be considered for both acid and amine fold models, each with either swelling agent. For convenience, these situations will be labelled ACH and ACD for acid fold crystals with hydrogenous and deuterated swelling agents and AMH and AMD for amine fold crystals with the same two swelling agents.

The scattering length density profile for an individual lamella with either acid or amine folds can be considered as the convolution of a single block (either acid or amine) with an arrangement of points. Figure 3 shows the example of the AMD model. Here, the function f₅ has half the thickness of the amine block, and is convoluted with functions representing three pairs of points f₂, f₃ and f₄. The scattering function can then be obtained by multiplying together simple sinusoidal and sinc functions.

Some general features emerge without detailed calculations. First, models AMH and ACD differ only in the size of the repeat unit, as can be seen using Babinet's principle. From the scattering lengths listed in Table 1, the lower scattering length density amine block is clearly narrower than the acid block. If either block is represented by a rectangular scattering length density profile,

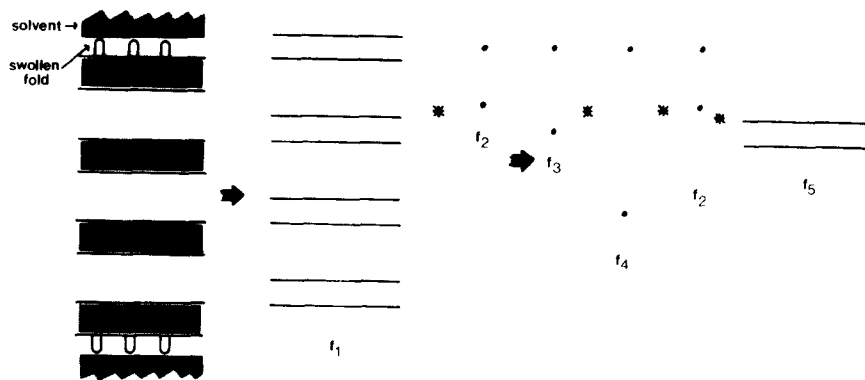


Figure 3 Schematic representation of a d_8 -6,6-nylon lamella with amine folds, swollen with deuterated solvent (left). The structure can be represented as a convolution (*) of the two functions f_1 and f_2 , which in turn can be represented as a convolution of functions f_3 , f_4 , f_2 and f_5 .

then the scattering is simply described by a sinc function, decaying more rapidly for model ACD. The effect on the 001 peak position is, however, relatively minor. The major difference between AMD and ACH models is again the block width, with the 001 peak shifting to higher angles with decreasing block width.

CALCULATED DIFFRACTION PATTERNS

The subcell structure of 6,6-nylon is well known⁶. For crystals grown under the conditions described here, the observed X-ray long spacing is $\approx 54 \text{ \AA}$, corresponding closely to four times the (001) spacing (51.2 \AA)³. Using the scattering lengths in *Table 1* and a one-dimensional array of atomic positions, the scattering function can be readily calculated. However, as a first approximation, we take a simple 'block' model of the scattering length profile, as in *Figure 2*. Scattering functions for lamellae with acid folds only and amine folds only are shown in *Figure 4*. The lamellae are considered here as isolated units, without swelling agent. Despite these simplifications, the scattering is clearly sensitive to fold type, with a significant shift in position and change in width of the 001 peak. Although the diffraction pattern is more drastically changed away from the 001 peak, it was found practicable only to obtain an adequate signal:noise ratio near the 001 peak (see below). For this reason, we will eventually focus our attention on the 001 peak.

The plots show several differences from the analogous X-ray calculations^{3,4}. Most evident is the reduction in the 002:001 amplitude ratio for the neutron scattering case. The number of subsidiary maxima changes from two for the amine fold model to three for the acid fold model. This can be understood by again considering the structure as the convolution of several functions. Both models share the element of a four-unit repeat, but this must be convoluted with different functions for the two different fold models. For the amine fold, the second function is simply a top-hat function, arising from the acid blocks. The situation is more complicated for the acid fold, where it is necessary to convolute a 'top-hat' function, corresponding to half an acid block, with a pair of points separated by the repeat distance minus half an acid block. The significance of the latter contribution to the Fourier transform is to introduce a periodicity of 0.2 \AA^{-1} and to give rise to a zero crossing at $\frac{3}{4} \times 0.2 \text{ \AA}^{-1} = 0.15 \text{ \AA}^{-1}$. This falls within the 002 peak

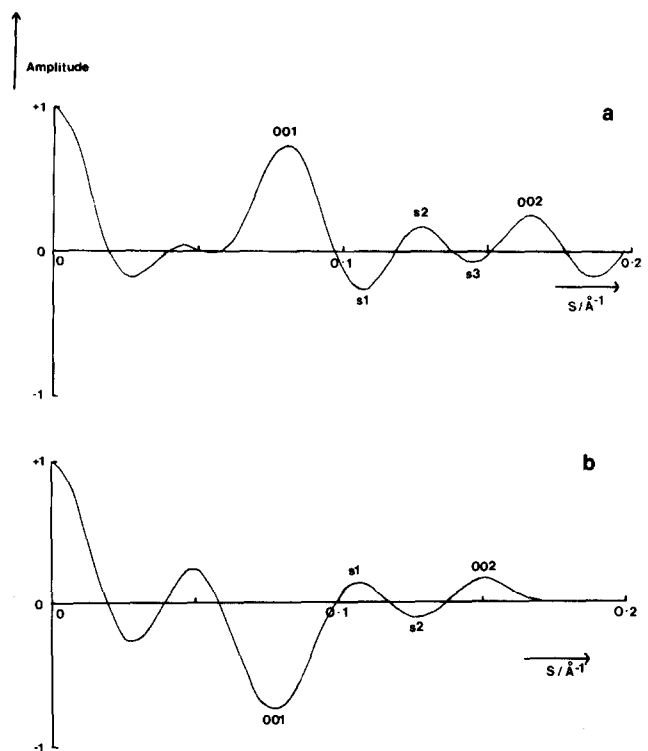


Figure 4 Scattering functions calculated using a simple 'block' model to describe variations in scattering length: (a) acid fold model; (b) amine fold model

profile, splitting the peak into two (*Figure 4a*) and thereby introducing an additional subsidiary maximum (S_3), inside the main 002 peak.

It is therefore not possible, through the neutron scattering experiment, simply to use the number of subsidiary maxima as a direct indication of the crystal thickness, although in principle the number itself may provide an indication of fold type.

Returning to the full molecular model, using the established atomic co-ordinates and scattering lengths, we have calculated scattering intensities for models ACH, ACD, AMH and AMD. As indicated earlier, our main interest is in the 001 Bragg reflection, as a result of the low intensities of subsidiary peaks. Experimentally, the shift in position of the 001 peak with change in isotopic labelling of the solvent can be determined to greater

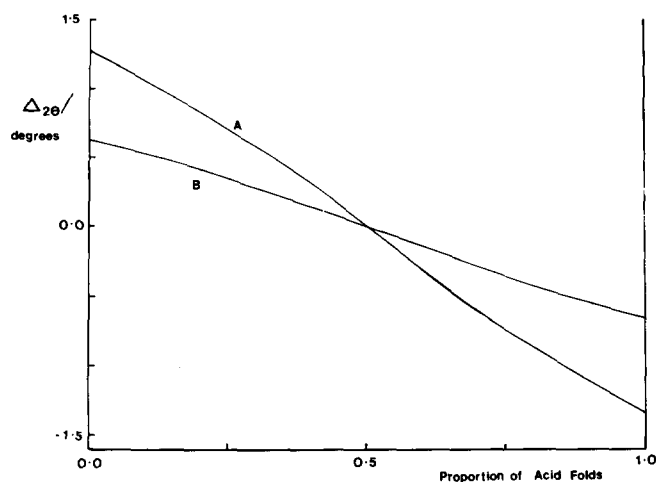


Figure 5 Calculated shifts in 001 peak position on changing from hydrogenous to deuterated swelling agent: A, neutron wavelength = 4.7 Å; B, 2.35 Å

precision than the absolute peak positions. It is, therefore, more informative to take a single sample and record its diffraction pattern using hydrogenous and deuterated swelling agents. We have calculated the shift in peak position on changing swelling agent, for both acid or amine fold structures. The effect of a mixture of fold types was also considered, with the assumption that individual lamellae have a single fold type. It was noted above that the narrow fold layer appears to preclude less regular folding. In this case, the diffraction intensities from separate crystals, and hence from separate structures with acid and amine folds, will be additive. To provide a direct comparison with neutron scattering data, the function I/θ^2 was calculated for each model (I = intensity, 2θ = scattering angle) and the shift in peak position of this function with change in swelling agent ($\Delta_{2\theta}$) was calculated. The results are shown in Figure 5 for the two experimental wavelengths. The predicted shifts are appreciable for models approaching 100% amine folds ($+1.26^\circ$ for $\lambda = 4.7 \text{ \AA}$) or 100% acid folds (-1.34° for $\lambda = 4.7 \text{ \AA}$), but decline to zero, as expected, for equal proportions of fold types. The method thus provides a sensitive indicator of the proportion of fold types.

EXPERIMENTAL

Partially deuterated 6,6-nylon salt was prepared by mixing ethanolic solutions of d_8 -adipic acid (Merck, Sharp and Dohme) and hexamethylene diamine. The washed and dried precipitate was polymerized in the usual manner, by heating at 270°C (see, for example, reference 7).

Single crystals were grown from a dilute solution of d_8 -6,6-nylon in butane 1,4-diol at 120°C . Filtration was carried out with heating, to avoid crystallization on cooling. The slurry was washed with butanone and a mat prepared with the slurry sandwiched between filter papers and slight applied pressure. This results in a mat with preferred lamellar orientation in the mat plane. Mats were dried and cut into thin ($\approx 1 \text{ mm}$ wide) strips.

Neutron scattering experiments

Two instruments were used, with differing neutron wavelengths:

(1) the Guide Tube diffractometer⁸ (AERE, Harwell), with Soller collimation and a single detector, wavelength 4.7 Å; and

(2) the HB-IA triple-axis spectrometer (Oak Ridge National Laboratory, Tennessee), wavelength 2.35 Å.

In each case, samples were mounted in stacks, with the mat normal perpendicular to the incident beam. Either butane 1,4-diol or d_8 -butane 1,4-diol was used to swell the crystals, with Soxhlet extraction using butanone and thorough drying between measurements. The sample holder was covered with a thin aluminium can to prevent excessive evaporation during the long scan times ($\approx 5 \text{ d}$) for the Guide Tube diffractometer. In addition, cadmium shielding was used to mask the samples. Bismuth was used to calibrate the Guide Tube diffractometer.

A background signal was subtracted before determining 001 peak positions in each case. A smooth curve was used to match intensities on either side of the 001 peak. Since we are primarily concerned with the peak position rather than its intensity, the error introduced is believed to be small in relation to the possible range of values for $\Delta_{2\theta}$ (Figure 5).

RESULTS

Data collected using the Guide Tube diffractometer are shown in Figure 6 for hydrogenous and deuterated swelling agent. The low angle diffraction peak yields long spacings of 77 and 82 Å in the two cases, respectively, in line with previous X-ray measurements³. Despite the addition of butane 1,4-diol, higher orders of the low angle peak persist, particularly in the case of deuterated

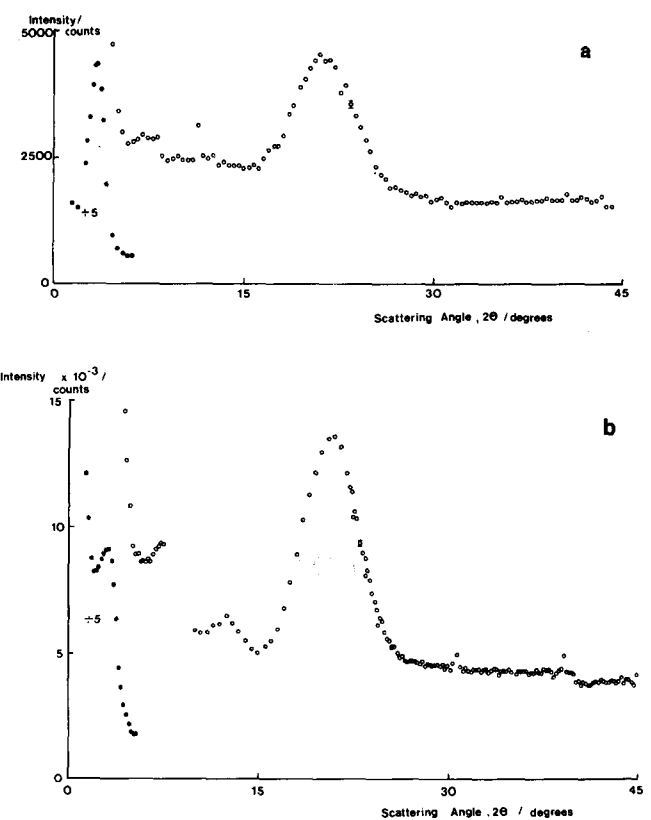


Figure 6 Neutron scattering data obtained using the Guide Tube diffractometer (Harwell) with (a) hydrogenous and (b) deuterated swelling agent. The long spacing is shown on a reduced scale in each case

Table 2 Effect of change of swelling agent on 001 peak position

Neutron wavelength (Å)	$\Delta_{2\theta}/(\text{deg})^a$	Proportion of acid folds ^b
4.7	-0.6 ± 0.3	0.7 ± 0.12
2.35	-0.8 ± 0.04	0.55 ± 0.03

^aChange in scattering angle (2θ) on changing from hydrogenous to deuterated swelling agent

^bAs determined using the calibration curves, Figure 5

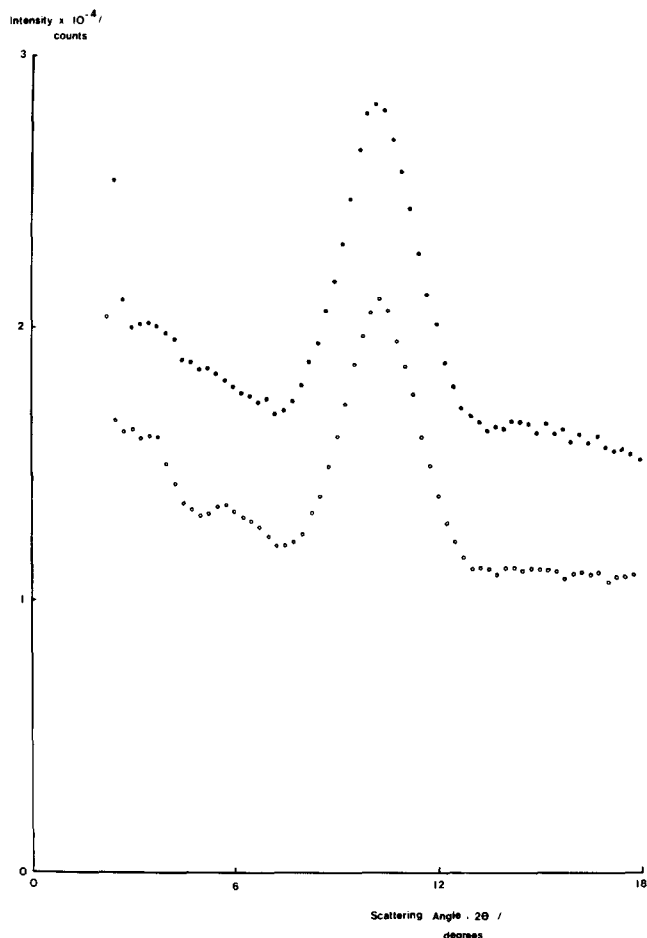


Figure 7 Neutron scattering data from the HB-IA spectrometer (Oak Ridge) for hydrogenous (●) and deuterated (○) swelling agent

swelling agent. However, there is little indication of subsidiary maxima beyond the 001 Bragg reflection. As mentioned above, the subsidiary maxima have low predicted intensities, and the counting statistics in Figure 6 are clearly inadequate for making intensity measurements on them. After subtraction of a background signal, the 001 peak position was determined and the results are shown in Table 2. The observed shift in peak position ($\Delta_{2\theta} = -0.60^\circ$) was then used with Figure 5 to determine a proportion of 70% acid folds.

Diffraction data from the HB-IA spectrometer are shown in Figure 7 before background subtraction. Again, higher orders of the low angle peak are seen, especially with the deuterated swelling agent. The subsidiary maxima are also unsuitable for intensity measurements. The shift in 001 peak position is shown in Table 2, leading to an estimate of 55% for the proportion of acid folds present. Note that the fold proportion figures obtained

from the two instruments are in agreement to within the estimated experimental errors.

DISCUSSION

The experimental results presented here indicate a proportion of acid folds within the 6,6-nylon single crystals studied of $\approx 58\%$. A comparison between this result and previous analogous X-ray diffraction measurements is clearly necessary, but first some differences between the two techniques, should be noted. The X-ray method^{3,5} was based on measurements of the relative intensities of subsidiary maxima in the diffraction data. The importance of the correct choice of background intensity was recognized at an early stage³ and later used in analysing the diffraction patterns from solution annealed samples⁵. In the latter case (where the number of subsidiary maxima has increased to three), different backgrounds were drawn under the subsidiary peaks, with the intention of bracketing the correct background. The measured peak intensity ratios supported a model with the acid fold favoured, but the estimated extent of this predominance was found to vary with the background chosen. No numerical estimates were given for the proportion of acid folds, but the general conclusion was that a strong preference existed for acid folds, in agreement with earlier work on solution-grown crystals in the unannealed state (where two subsidiary maxima are observed)³.

By contrast, although the present work was started with the aim of studying relative intensities of subsidiary maxima, it emerged that another effect dependent on fold type, namely the shift in position of the 001 peak with change in isotopic species for the swelling agent, was more readily measured by neutron diffraction. This shift in peak position has also been calculated for various proportions of the different fold types to allow a quantitative estimate of the proportion of acid folds. For the crystallization conditions considered here, the results from X-ray diffraction and neutron scattering measurements are in agreement, in that they both indicate a predominance of acid folds. Although previous X-ray work has not provided a numerical estimate for the relative proportions, we have now obtained an estimate from neutron diffraction data.

It was noted above that infrared (i.r.) spectroscopy has previously indicated the presence of amine folds. An i.r. band at 1329 cm^{-1} was assigned⁴, on the basis of deuterium substitution⁹, to a specific regular fold conformation which appears to involve the amine group in 6,6-nylon. The decrease in intensity of the 1329 cm^{-1} band with increasing annealing temperature (for solution-grown crystals only) was attributed to the reduction in number of regular amine folds during annealing, whereas in bulk crystallized samples an increase in band intensity with increasing annealing temperature was attributed to the formation of progressively more regular folds. However, if both acid and amine folds can exist in separate lamellae, then the change in the proportion of amine folds during annealing may depend critically on the proportion in the original crystals. The absence of (or inability to detect) any i.r. band corresponding to the acid type of fold may not be remarkable. It has been suggested⁴ that the 1329 cm^{-1} band may arise from the interaction of the amide III band with wagging and twisting modes of the CH_2 groups. It is now well

established that CH₂ wagging modes in polymethylene chains can arise from specific isomeric states of the chain (see, for example, reference 10) or from strained configurations¹¹. The frequencies of these modes are conformationally sensitive, so that CH₂ wagging modes arising in the acid fold region of 6,6-nylon may be shifted from the observed amide fold band by the different adjacent chemical groups, by the absence of amide III coupling and also by conformational differences in the two types of fold.

CONCLUSIONS

Measurements of the 001 peak position in the neutron diffraction pattern of 6,6-nylon single crystals swollen with butane 1,4-diol show a shift on changing to deuterated swelling agent. The shift has been observed for two neutron wavelengths, and provides an estimate of 58% for the percentage of acid folds in the crystals, on the assumption that individual crystals uniformly involve one type of fold only. This slight preference for acid folds is consistent with previous X-ray measurements, which indicated a predominance of acid folds, although in this case quantitative estimates were not possible. Further infrared spectroscopy is necessary to establish whether fold bands from both amine and acid folds are present.

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