Diffraction pattern and structure of amorphous and crystalline regions in semicrystalline nylon 6.6

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X-ray diffraction data on two nylon 6.6 samples of different crystallinity are analysed to yield separate scattering functions for the amorphous and crystalline regions. The amorphous pattern is found to be quite different from the smooth background usually assumed in the determination of polymer crystallinity. Radial distribution functions derived from the data are qualitatively different beyond the nearest neighbour distance regions. The curves for the crystalline regions show discrete distance distributions to very large separations. In contrast, the positional correlation between atom pairs in the amorphous regions are short-range and much less well defined, and the degree of hydrogen bonding in the amorphous regions appears to be lower than in the crystalline regions.

(Keywords: nylon 6.6; structure; amorphous; crystalline; radial distribution functions; X-ray diffraction)

INTRODUCTION

Poly(hexamethylene adipamide) (nylon 6.6) crystallizes to form lamellar structures in which the chains are normal to the plane of the platelets[1]. The thickness of these lamellae is ~50–100 Å corresponding to up to six monomer units. In fact it has been shown[2] that there is an optimum number of three to four units per crystal, based on structural considerations. These numbers suggest chain folding in order to connect one crystal traverse (stem) with another. The structure of the crystalline portions of nylon 6.6 has been determined from an X-ray diffraction study of oriented fibres[3]. The repeat unit contains relatively long methylene sequences connected by the hydrogen-bonded amide groups. The crystal structure (*Figure 1*) is triclinic and the hydrogen bonds are disposed on planar sheets parallel to *a–c* planes. Very little is known about the structure of the non-crystalline (amorphous) portions which connect the crystal stems. This is because the diffraction pattern of semicrystalline materials is usually interpreted in terms of crystal reflections located on a uniform diffuse background. This background is then discarded because it does not lend itself to the standard crystallographic analysis.

We will show in this paper that the diffraction patterns of the crystalline and amorphous parts in semicrystalline polymers can be separated if at least two precise data sets from samples which differ only in their degree of crystallinity are measured. In the case of nylon 6.6 this method leads to self-consistent radial distribution functions for the crystalline and amorphous regions of the material. It also shows that the conventional method of treating the amorphous scattering as a smooth background is quite unsatisfactory.

BASIC CONCEPTS

The structure of a crystalline material is specified by the lattice parameters, the symmetry of the space group, and by the mean atomic positions in the unit cell, together with estimates of the amplitudes of thermal vibration of each of the nuclei. The periodicity of the lattice allows the construction of a model of the unit cell which is representative of the entire crystal. Most polymeric materials consist of small crystallites embedded in and connected by amorphous regions. Only if these crystallites become highly oriented, as in fibres, can crystallographic techniques usefully be applied to give a unique description of the overall structure. These methods become less useful as the degree of crystallinity decreases, and they are

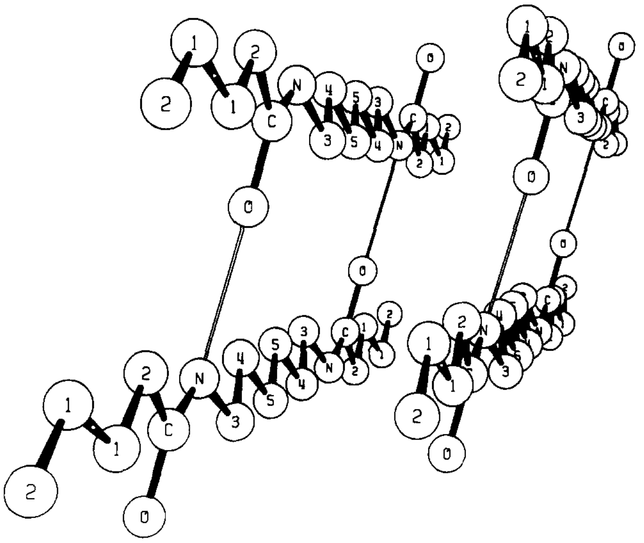

Figure 1 Structure of the crystalline region of nylon 6.6 at room temperature. The number of methylene groups is that of reference 3. Hydrogen atoms are not shown

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inappropriate for the description of amorphous and molten materials. Here the short-range order or structure is usually described by probability functions of the relative positions of the particles. These atom pair distribution functions $g(r)$ depend only on the scalar distance r between atom pairs, and are defined so that $\rho g(r)\,\mathrm{d}\underset{\sim}{r}$ is the average number of atoms in the volume element $\mathrm{d}\underset{\sim}{r}$ at a distance r from an origin atom. Radial distribution functions can be obtained from diffraction experiments on any macroscopically isotropic material. It may not be widely appreciated that this includes polycrystalline powders, as long as the crystallites are randomly oriented. We present in this paper X-ray diffraction data on semicrystalline powders of nylon 6.6. The data are analysed to yield structure functions which are then separated into the contributions from crystalline and amorphous regions.

Following our previous work on related materials[4–13], we consider nylon 6.6 as composed of $-CH_2$ and $-NH$ groups which are treated as single scattering sites, as well as C and O atoms. As a result, our work yields no information on interactions involving hydrogen which is difficult to obtain from one-dimensional X-ray scattering data anyway. On the other hand, since the group scattering factors for $-CH_2$ and $-NH$ were calculated from an expansion of the electron density about the C and N atoms as centres, information about these interactions will be obtained directly and unambiguously from the data. The atom pair distribution functions $g_{\alpha\gamma}(r)$ are related to the experimentally accessible structure functions $\hat{h}_{\alpha\gamma}(k)$ by the expression

$$\hat{h}_{\alpha\gamma}(k)=4\pi\int_0^\infty r^2 h_{\alpha\gamma}(r) j_0(kr)\,\mathrm{d}r \qquad (1)$$

with $h_{\alpha\gamma}(r)=g_{\alpha\gamma}(r)-1$, $j_0(x)=\sin x/x$, and $k=(4\pi/\lambda)\sin\theta$, the momentum transfer coordinate for elastic scattering of radiation of wavelength λ at an angle 2θ. A single X-ray diffraction experiment yields the structure function $H(k)$ which is a weighted sum of the functions $\hat{h}_{\alpha\gamma}(k)$.

EXPERIMENTS AND DATA REDUCTION

Sample preparation and characterization

Two samples of nylon 6.6 were prepared differing in their degree of crystallinity. Both samples were derived from pellets of melt-crystallized nylon 6.6 of approximate molecular mass 5000–20 000 g mol^{-1} (purchased from du Pont). For the first sample the melt-crystallized pellets were simply ground into a fine powder and used without processing. For the second sample some of the ground material was dissolved in ethylene glycol by heating at 180°C and then crystallized on slowing cooling. The concentration was $\sim 50\,\mathrm{g\,l^{-1}}$ and the precipitation temperature ~ 150°C. The gel produced was vacuum filtered and then washed with excess of doubly distilled water to remove the high-boiling ethylene glycol. The thick, wet powder obtained was then ground and dehydrated over P_2O_5 in a desiccator and finally dried in a vacuum oven at 100°C to produce a fine powder. This recrystallization resulted in a sample of higher crystallinity than the melt-crystallized sample. From the measured heat of melting the crystallinity of the samples was calculated as 47% for the solution-crystallized and 29% for the melt-crystallized materials. The heat of fusion of a completely crystalline sample was taken as 57.4 kJ mol^{-1} (ref. 14). The densities of the samples were calculated from the crystallinities by use of a linear interpolation between the published values[15] of the amorphous and crystalline densities of 1.096 and 1.213 g ml^{-1}, respectively.

Diffraction experiments

The X-ray measurements were made using reflection geometry[16] and monochromatic MoKα radiation (λ = 0.7107 Å). The range of scattering angles measured cover the interval $0.3<k<16$ Å^{-1}, with an increment of $\Delta k=0.02$. Counts ranging from 20 000 at the lowest to 500 000 at the highest angles were accumulated. Corrections for background, absorption[17], polarization, incoherent scattering[18], monochromator discrimination[16] and multiple scattering[19] were applied. The corrected cross-sections were normalized to the scattering from a single average site, $S_s(k)=\sum_\alpha f_\alpha^2$. The coherent scattering factors were taken from the International Tables for X-ray Crystallography and Table 1 of reference 7. The normalized scattering functions $S(k)$ for the two samples of nylon 6.6 thus obtained are shown in *Figure 2*. They are characterized by relatively sharp peaks extending to ~ 6 Å^{-1}, with damped oscillations around the independent site scattering curve, $S_s(k)$, beyond these momentum transfers.

Next, a structure function $H(k)$ was obtained according to

$$H(k)=M(k)[S(k)-S_s(k)] \qquad (2)$$

where the modification function chosen was $M(k)=[\sum_\alpha f_\alpha(k)]^{-2}$. The structure functions $H(k)$ are weighted sums of the partial structure functions defined in equation (1), namely:

$$H(k)=M(k)\sum_\alpha\sum_\gamma f_\alpha(k)f_\gamma(k)\hat{h}_{\alpha\gamma}(k) \qquad (3)$$

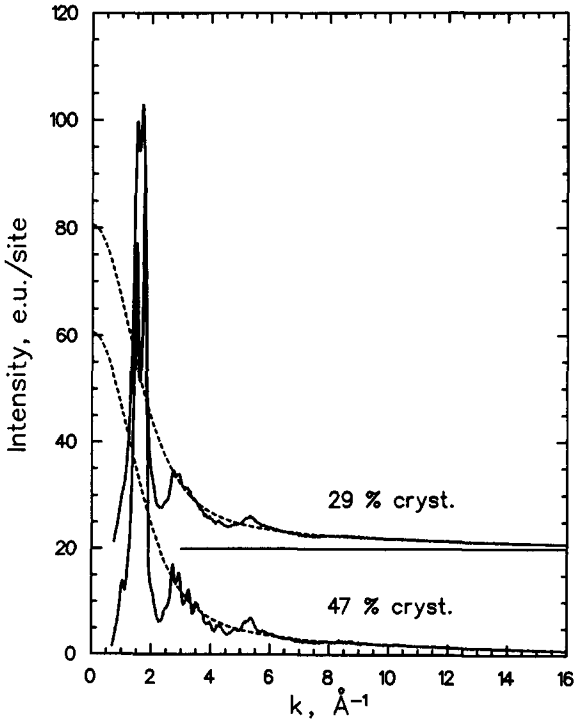

Figure 2 Measured coherent scattering function $S(k)$ (——) and the calculated self-scattering from independent sites $S_s(k)$ (– – –) for two semicrystalline samples of nylon 6.6

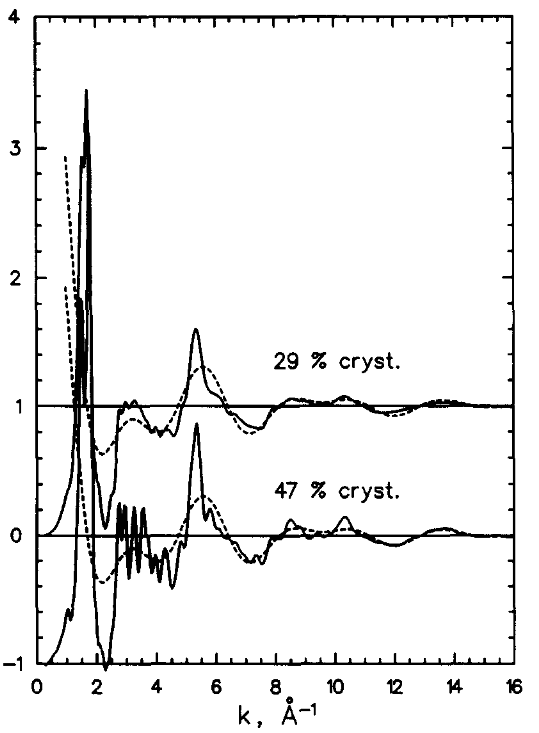

Figure 3 Structure functions for two semicrystalline samples of nylon 6.6 derived from X-ray scattering. Both curves approach the theoretical curve for the scattering from the rigid near-neighbour distances with increasing values of the momentum transfer k. ——, $H(k)$; – – –, skeletal model

Table 1 Parameters used to calculate the structure function for the skeletal distances[3] in nylon 6.6 using the Debye equation as described in reference 20

Distance	r (Å)	Distance	r (Å)
$\mathrm{CH_2}$(1)–$\mathrm{CH_2}$(1)	1.56	$\mathrm{CH_2}$(1)--$\mathrm{CH_2}$(2)	2.66
$\mathrm{CH_2}$(1)–$\mathrm{CH_2}$(2)	1.55	$\mathrm{CH_2}$(3)--$\mathrm{CH_2}$(5)	2.42
$\mathrm{CH_2}$(3)–$\mathrm{CH_2}$(4)	1.48	$\mathrm{CH_2}$(4)--$\mathrm{CH_2}$(5)	2.51
$\mathrm{CH_2}$(4)–$\mathrm{CH_2}$(5)	1.55	$\mathrm{CH_2}$(1)--C	2.45
$\mathrm{CH_2}$(5)–$\mathrm{CH_2}$(5)	1.53	$\mathrm{CH_2}$(3)--C	2.46
$\mathrm{CH_2}$(2)–C	1.50	$\mathrm{CH_2}$(2)--NH	2.40
$\mathrm{CH_2}$(3)–NH	1.48	$\mathrm{CH_2}$(4)--NH	2.36
C=O	1.35	$\mathrm{CH_2}$(2)–=O	2.53
C–NH	1.38	NH–=O	2.37
NH–O′	2.78	$\mathrm{CH_2}$(1)--=O	2.79
		$\mathrm{CH_2}$(3)--=O	2.82

The numbering of the methylene groups is that of reference 3

The functions $H(k)$ derived from the data are shown in *Figure 3*. Also shown is a calculated[20] curve for the so-called 'skeletal' atom pair distances. The skeletal atom pair distances in the present case include all the distances between directly bonded atom pairs and the distances between atom pairs connected through a single third atom. These skeletal distances are independent of conformation, and in particular they should be the same in both the crystalline and amorphous regions of nylon 6.6. The skeletal distances for nylon 6.6 are in the range 1.4–1.5 Å for the bonded atom pair distances, and 2.4–2.5 Å for the atom pair distances separated by a third atom (*Table 1*). It is apparent upon inspection of *Figure 3*, that, with increasing k, the structure functions for the two nylon 6.6 samples approach each other and the curve calculated for the skeletal distances.

Separation of crystalline from amorphous structure

It is to be expected that the structure of the amorphous portion of a polymer is different from that of the crystalline part. In order to separate the crystalline from the amorphous structure, the assumption of a strictly two-phase model has to be made. This assumption implies that the transition between the crystalline and amorphous regions is abrupt. With this two-phase model we can write the structure function $H(k)$ derived from diffraction data on a material consisting of a crystalline fraction c and an amorphous fraction $(1-c)$ as

$$H(k)=cH_c(k)+(1-c)H_a(k) \tag{4}$$

where $H_c(k)$ and $H_a(k)$ are the structure functions for the crystalline and amorphous regions, respectively. It is clear from equation (4) that the quantities $H_c(k)$ and $H_a(k)$ can be determined from two diffraction experiments with samples which differ only in the crystallinity c.

We have solved equation (4) using the two structure functions shown in *Figure 3* and the crystallinities obtained from the measured heats of melting. The structure functions for the amorphous and crystalline regions thus obtained are shown in *Figure 4* to values of $k=8$ Å^{-1}. At larger momentum transfers the two curves become very nearly equal to each other and to the curve calculated for the skeletal distances, as shown in *Figure 3*. This large k behaviour is an important test of the internal consistency of the results obtained from our analysis.

Fourier inversion of the structure functions thus derived yields radial distribution functions

$$G(r)=1+(2\pi^2\rho r)^{-1}\int_0^\infty kH(k)\sin(kr)\,\mathrm{d}k \tag{5}$$

From equation (3), it is seen that $G(r)$ is a weighted sum

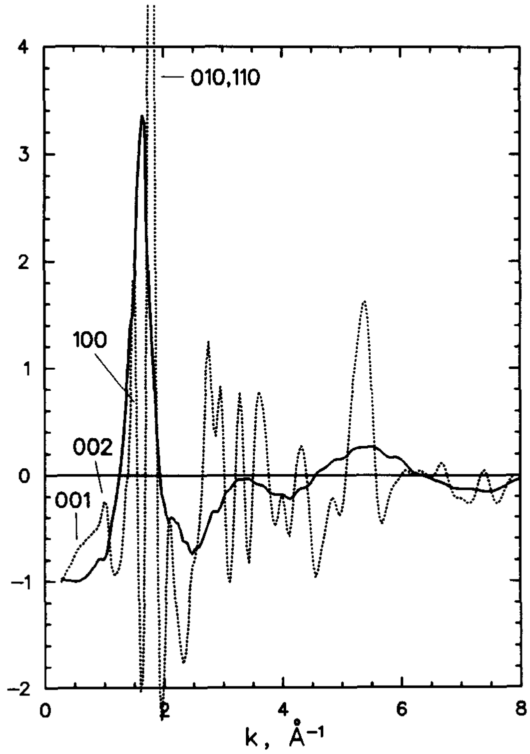

Figure 4 Structure functions for the amorphous (——) and crystalline (– – –) regions in nylon 6.6. The range of momentum transfers shown corresponds to the angular range $0<2\theta<158°$ for the widely used CuKα radiation

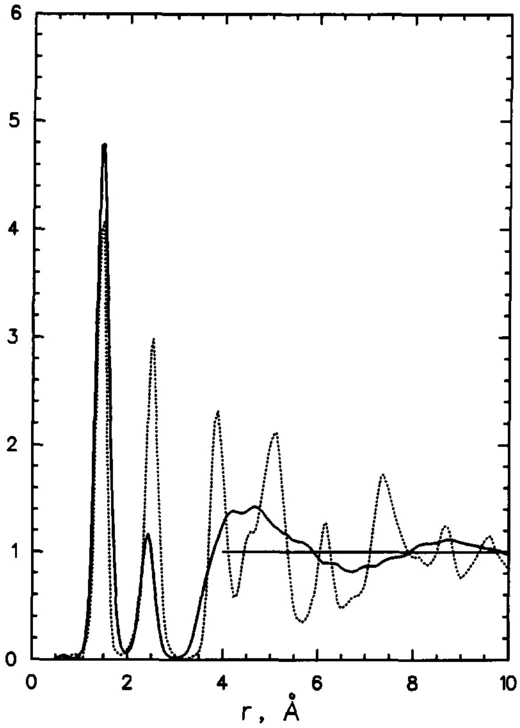

Figure 5 Radial distribution functions for the amorphous (——) and crystalline (---) regions in nylon 6.6. The distinct long-range features from extended chains present in the crystals are absent in the amorphous regions

of site–site distribution functions $g_{\alpha\gamma}(r)$ modified by products of the scattering factors. The modification is minimal because of our choice of sites—the scattering factors for CH_2, NH, C and O sites are very similar, and hence the products $f_\alpha(k)f_\gamma(k)M(k)$ in equation (3) are very nearly independent of the variable k. The functions $G(r)$ are mainly of use in identifying the peak locations of the dominant site–site correlations. In practice, the Fourier inversion of diffraction data can result in radial distribution functions which contain unphysical features because the integral in equation (5) is terminated at finite values of the variable k and the usual inversion algorithms transmit systematic and random errors. In the present work the functions $G(r)$ were obtained using a maximum entropy (ME) algorithm[21] which attempts to minimize the transfer of errors in the measured data to the distribution function. In effect, a function $G(r)$ is modelled which (i) is as consistent as possible with the measured function $H(k)$, (ii) satisfies known limits, i.e. $G(0)=0$ and $G(\infty)=1$, (iii) has the least amount of structure compared to all the distributions which satisfy (i) and (ii). The main advantages of the ME algorithm over the traditional method of direct Fourier transform are that statistical noise is not reproduced and the data are extended smoothly and with minimum bias into regions of k where no measurements are available. The radial distribution functions thus obtained are shown in *Figure 5*. These curves are weighted averages of the distances involving C, N and O atoms.

RESULTS AND DISCUSSION

The structure of crystalline nylon 6.6 is known from fibre diffraction[3], and the sharp Bragg peaks in the curve for the function $H_c(k)$ in *Figure 4* can be accounted for in crystallographic terms. The first four peaks correspond to the (0 0 1), (0 0 2), (1 0 0) spacings and the (1 1 0), (0 1 0) doublet. The first two peaks are due to order along the polymer chain, and their intensities are quite small. The reason is that one crystal stem contains only three to four repeat units. The two strong peaks are due to lateral order. The (0 1 0) peak, characteristic of the hydrogen-bonded *a–c* planes, is larger than the peak for the (1 0 0) spacings. This indicates a high degree of hydrogen bonding in the crystallites.

The curve for the amorphous regions shows a prominent peak followed by continuous damped oscillations. The first amorphous peak is located between the strong lateral reflections of the crystalline material. This feature is found in the diffraction patterns of many non-crystalline solid and liquid hydrocarbons, and has been the subject of much speculation. It does however, not lend itself to any simple physical interpretation[22]. The amorphous diffraction pattern (*Figure 4*) shows much more structure than usually assumed. This finding casts doubts on the procedure typically employed in calculations of crystallinity in polymers from X-ray diffraction: the subtracted amorphous background is always considered to be broad and structureless, in contrast to the pattern obtained here.

The radial distribution functions for the crystalline and amorphous regions derived from the curves of *Figure 4* are shown in *Figure 5*. The peak near 1.5 Å corresponds to the C–C, C–N and C=O bond distances which are very nearly equal in the curves for the crystalline and amorphous regions. These bond distances do not depend on the conformation and are, thus, expected to be the same for the crystalline and amorphous regions. In fact, the area under both these peaks corresponds to about two neighbours for an average site. The peak near 2.5 Å, where the remaining skeletal distances are expected, is larger in the curve for the crystalline regions, especially on the longer distance side. The respective areas under these peaks correspond to about 1.5 neighbours for the amorphous and 3.5 neighbours for the crystalline regions. There are two possible contributions to a larger coordination number for the 2.5 Å peak in the crystalline region curve. First, in a strictly planar chain there is a distance at 2.8 Å (the $CH_2(1)$—=O distance, see *Table 1* and *Figure 1*) which is not necessarily present in the amorphous region, due to possible rotation about the $CH_2(2)$–C bond. The second possibility is that there are more NH···O hydrogen bond distances (at 2.8 Å) contributing to the 2.5 Å peak in the crystalline curve than in the amorphous curve, implying, for example, that if the crystalline regions are fully hydrogen bonded, the amorphous regions are less so. Unfortunately, these 2.8 Å contributions are not resolved from the broad distribution of skeletal distances at 2.5 Å. They do however, seem to occur less frequently in the curve for the amorphous regions.

An additional observation is the lack of a distinct *gauche* peak near 3 Å in $G_a(r)$, the curve for the amorphous regions. This can be interpreted in terms of a broad distribution of distances about the value expected for the *gauche* conformation. Such a broad distribution can be expected in the amorphous regions below the glass transition. We caution that the observed lack of resolved hydrogen bond and *gauche* peaks in the curves for the amorphous regions has to be regarded within the uncertainty of the data.

At longer distances the curves for the two regions differ even more drastically. Crystalline nylon 6.6 shows the discrete distances typical of the long range order in a crystalline material, starting at 3.9 Å and extending to very large distances. The curve for the amorphous regions shows broad peaks near 4–5 and 9 Å with a uniform distribution of distances, i.e. no structure beyond ~15 Å. This lack of correlation much beyond second and third neighbour chains is also typical of amorphous materials.

We have shown that the collection of high-precision diffraction data and their reduction to structure functions on an absolute scale allows us to obtain information not usually available for polymers. Small differences in the measured patterns have been interpreted and exploited to provide structure and radial distribution functions for fully amorphous nylon 6.6 samples. The success of the analysis is only contingent upon the assumption of a two-phase model for the crystalline and amorphous regions of the polymer. This assumption, always made in polymer crystallography, does not necessarily limit our new method: it is quite feasible to derive the same information for a three-phase model from three sets of high-precision diffraction data.

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