

Structure of acrylic fibres prior to cyclization

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The phase structure and thermal transition of acrylic fibres have been investigated at several temperature increments from 22 to 200°C. Two glass transition temperatures at 82 and 140°C have been identified and corresponded to the structural transitions of the paracrystalline and amorphous regions, respectively. These experimental observations give strong evidence to support the 'limited two-phase' model. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

High temperature wide-angle X-ray diffraction (HTWAXD) studies on polyacrylonitrile (PAN)-based fibres were reported first by Bohn *et al.* in 1961¹, then by Hinrichsen in 1972², and later by Jiang *et al.* in 1987³. Bohn *et al.* reported changes in both the polymer volumetric expansion coefficient and the temperature dependence of 5.2 Å *d*-spacing at 85°C. This observation together with the absence of the characteristic amorphous scattering halo in the fibre X-ray patterns supported a single-phase paracrystalline morphology in which each chain fitted into a 0.6 nm diameter cylinder and assumed a more or less rigid, twisted, kinked and irregular helical conformation. These cylinders were closely packed parallel in a hexagonal form. Hinrichsen, on the other hand, observed two distinct steps of thermal expansion derived from the equatorial reflection of the 5.2 Å *d*-spacing. The first step of thermal expansion was between room temperature and 50°C and the second at 110°C. These two steps were interpreted as being associated with two different levels of atomic order, and were therefore used to support the two-phase morphology for PAN-based fibres. In studying the structural changes of PAN fibres during oxidation, Jiang *et al.* observed only one step at 95°C and used it to support a modified model of two-phase structure. To date, reports on thermally induced structural changes in PAN-based fibres remain inconsistent. The aim of this work is to gain further understanding of the thermal behaviour, structural transitions, and phase structure of PAN-based fibres. For PAN-based fibres, chemical changes, such as cyclization and dehydrogenation, are known to take place at temperatures above 180°C⁴. Therefore, the studies on the thermal behaviour of the lattice constant are focused on temperatures up to 180°C. A high temperature wide angle X-ray diffractometer (HTWAXD) was used. The advantage of an up-to-date HTWAXD is that it has more precise temperature control for accurate observation of thermal transitions, thus characterization of phase changes. Peak intensity and peak width data are also analysed to yield additional information on the fibre structure.

The acrylic fibres used in this study were Acrylan in the form of plain weave fabrics (Monsanto). A Scintag XDS 2000 X-ray diffractometer equipped with a high-temperature chamber was used. The CuK_α radiation was generated at an accelerating potential of 45 kV and a tube current of 45 mA. Filtration of the K_β radiation was provided by a single channel analyzer. The temperature in the chamber is measured by Wolfram/Rhenium 75/25 thermocouples. The sample was clamped directly to the heater which also served as a sample carrier to minimize the temperature gradient between the heater and the sample. The control for heating was fully automated with a ±1°C precision. The X-ray scanning was performed at 22 and at 25°C increments between 50 and 200°C. A heating rate of 5°C min⁻¹ was used to reach each target temperature. The fibres were maintained at the temperature for 10 min before X-ray scanning from a 14 to 19° 2θ range. Diffraction intensities were counted at 0.05° per step and the scanning time of each step was 2 s. The experimental data were analysed by employing multi-peak resolution methods⁵.

The HTWAXD patterns of the acrylic fabrics at varying temperatures between 22 and 200°C were collected. Each peak in the diffraction patterns was resolved in terms of peak height, peak width at half maximum height, and peak position. *Table 1* summarizes the resolved peak parameters of the acrylic fibres at the varying temperatures. In a hexagonal system, the corresponding lateral lattice constant can be calculated as

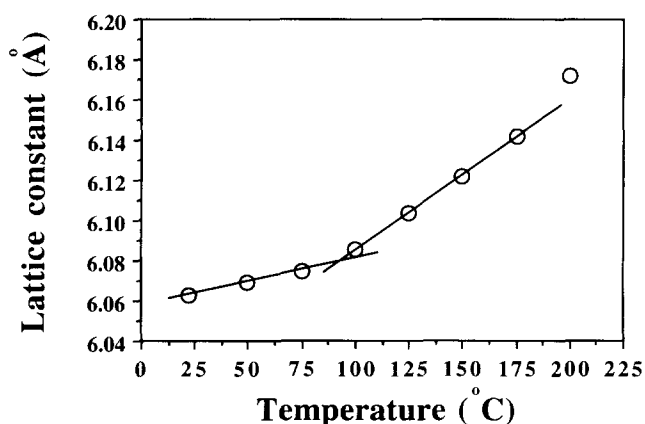
$$a = \frac{2d_{100}}{\sqrt{3}}$$

where *d*₁₀₀ is the *d*-spacing of the (100) peak which is calculated using Bragg's equation. The lattice constant increased with increasing temperatures between 22 and 200°C (*Figure 1*). It appeared that the lattice constant expanded first at the rate of 2.3 × 10⁻⁴ Å°C⁻¹ and then at the rate of 7.6 × 10⁻⁴ Å°C⁻¹. The two expansion rate lines intersect at 92°C, indicating a distinct change in thermal expansion of the lattice constant (*Figure 1*). Since the step reflects the peak position as a function of temperature, it is associated with the ordered regions in the acrylic fibres.

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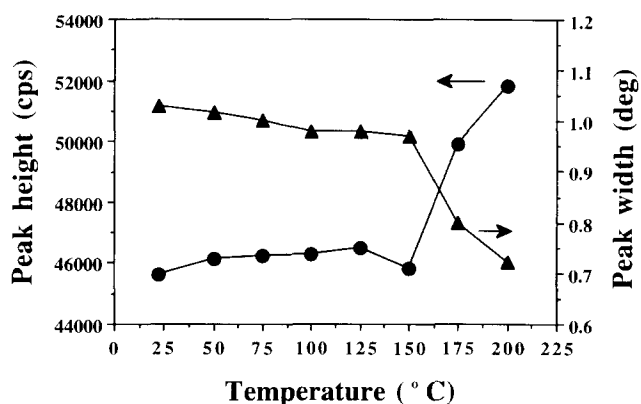
Table 1 Parameters of the resolved (100) peak

Temperature (°C)	<i>d</i> -spacing (Å)	Crystallite size ($\langle L_{100} \rangle$) (Å)
22	5.25	73.7
50	5.26	74.7
75	5.26	75.9
100	5.27	77.4
125	5.29	77.4
150	5.30	78.2
175	5.32	94.8
200	5.35	105

**Figure 1** Lateral lattice constant of the acrylic fibres at varying temperatures

It should be noted that an approximate 10° temperature gradient exists between the thermocouple and the sample surface upon which the X-ray impinges. This temperature gradient was simply obtained by running high temperature wide angle X-ray diffraction on polyethylene and poly(ethylene terephthalate) fibres and comparing their melting points with those detected by thermal analysis techniques such as differential thermal analysis. Therefore, the obtained step is actually at about 82°C. The expansion rates calculated here are higher than Jiang *et al.*'s ($8.3 \times 10^{-5} \text{ Å}^\circ\text{C}^{-1}$ above 95°C and $2.1 \times 10^{-4} \text{ Å}^\circ\text{C}^{-1}$ below 95°C) but lower than the values determined from the graph in Bohn's paper ($5.5 \times 10^{-4} \text{ Å}^\circ\text{C}^{-1}$ above 85°C and $1.1 \times 10^{-3} \text{ Å}^\circ\text{C}^{-1}$ below 85°C).

The X-ray diffraction intensities fluctuated slightly between 22 and 150°C, then increased dramatically from 150 to 200°C (Figure 2). Generally, X-ray diffraction intensities of polymers are expected to decrease with increasing temperatures, since the atoms oscillate around their zero positions with their oscillation amplitudes rising as a function of temperature. In contrast, the X-ray intensity in this work increased drastically at temperatures exceeding 150°C. The peak width decreased slightly with increasing temperatures between 22 and 150°C, then decreased sharply above 150°C. The peak width is associated with both the crystallite size and crystallite perfection. These data show that the crystallite size perpendicular to the (100) planes increase as a function of temperature. Both the increased X-ray intensity and decreased peak width with a distinct step near 140°C (10°C temperature gradient mentioned above) indicate that a more ordered structure in the fibres has been developed. This observation suggests that

**Figure 2** Influence of temperature on the peak height and the width at half height of the acrylic fibres

a structural transition from a disordered structure or the quenched state to a more ordered structure occurs at 140°C. This step is considered as the transition temperature from a disordered structure to the paracrystalline structure.

This work shows evidence of both paracrystalline and amorphous phases. The difference in order between these two phases is much less pronounced than that in the conventional two-phase model. It is interesting to note that the transition temperature for the amorphous regions is higher than that for the more ordered regions. This is so because the forces between the chains in the paracrystalline regions of acrylic fibres are summations of van der Waals and the random nitrile group interactions while the forces in the amorphous regions also include the much stronger dipole attraction of the nitrile groups. The chain conformation necessary to achieve dipole attraction is more random than that in the paracrystalline regions. Because of the very strong dipole attraction between the nitrile groups, the chain segments in the amorphous regions are stiffer than those in the paracrystalline regions.

The step in thermal expansion of the lattice constant derived from peak position in this work is consistent with that reported by Bohn *et al.*¹ but is lower than that proposed by Jiang *et al.*³. In addition, another step derived from peak height and peak width is identified. The two distinct steps reported by Hinrichsen, namely between room temperature and 50°C and at about 110°C, are not observed in this work. Our results are also in good agreement with those obtained by other methods such as dynamic modulus analysis⁶⁻¹⁰. Therefore, we have shown that the number and type of phase transitions can be determined using high temperature wide angle X-ray diffraction. In this way, the thermal behaviour and phase structure during heating can be depicted simultaneously.

The thermal behaviour, structural transitions, and phase structure of acrylic fibres have been investigated using high temperature wide angle X-ray diffraction techniques. The lateral lattice constant of the acrylic fibres increase non-linearly as a function of temperature between 22 and 200°C, with a distinct step at 82°C. This is the glass transition for the paracrystalline regions. The temperature influence on X-ray intensity or width of the reflection has revealed another structural transition near 140°C. This is the glass transition temperature for the amorphous regions. PAN molecules in the amorphous

regions have a more random, but stiffer conformation, than those for the paracrystalline regions because of the very strong dipole attraction between the nitrile groups. Therefore, the glass transition temperature for the amorphous structure is higher than that for the paracrystalline structure. The results of this work provide strong evidence to support the 'limited two-phase model' where the difference in order between the two phases is less pronounced than that in the conventional two-phase model¹¹.

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