

Oxidative stabilization of acrylic fibres

Part 3 *Morphology of polyacrylonitrile*

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A new model for the structure of oriented acrylic fibres is presented. The polyacrylonitrile molecules (or the acrylic sequences in a co-polymer) are suggested to form two distinct regions within a fibril: amorphous (disordered) and partially ordered. In the partially ordered regions, the polymer molecules assume a contorted helical shape to form rods with a diameter averaging about 6.0 \AA in which the nitrile units are oriented at various angles to the rod axis, but are spaced irregularly on or near the surface of the rod. The nitrile groups of adjacent rods can interpenetrate to form dipole pairs. The rods are ordered into a liquid crystal-type array, giving in some cases a lamellar-like texture oriented perpendicular to the fibril axis, with the ordered lamellae regions interspersed with amorphous regions. Evidence for the structure is obtained from transmission electron microscopy observations, a transient peak observed in small-angle X-ray scattering when fibres are thermally treated, as well as wide-angle X-ray diffraction patterns. The proposed model is consistent with the absence of a periodic repeat unit along the chain direction, with the $hk0$ reflections seen in wide-angle X-ray and electron diffraction, with the spherulitic morphology reported in some studies, and with the plate-like morphologies obtained under some conditions of precipitation from dilute solution.

1. Introduction

The structure of polyacrylonitrile and acrylic co-polymers has been the subject of many publications. When the bulk polymer is oriented, intense equatorial wide-angle X-ray reflections are observed which correspond to spacings of approximately 3.0 and 5.3 \AA measured normal to the chain direction, but the off-equatorial reflections are diffuse. This result has been interpreted by some workers as indicating that a definite repeat distance along the polymer chain does not exist. The morphology has been considered by some as that of single-phase laterally ordered polymer [1]; has been ascribed a planar unit cell and called a two-dimensional crystal by others [2–4]; and has been described as a paracrystalline, liquid crystal

texture by still others [5, 6]. Other authors take the position that three-dimensional crystallinity does exist in polyacrylonitrile, and have defined an orthorhombic unit cell [7–9] or a hexagonal unit cell [10].

The situation is further confused because under certain conditions the polymer can assume a spherulitic morphology [3] or even a "single crystal" plate-like texture [7, 9]. In the latter electron diffraction from the platelets shows only reflections of the $(hk0)$ type [2, 7, 9], again suggesting the lack of order along the chain axis. All of the studies cited have been conducted on polymers prepared by free-radical initiation. Polymers so prepared have been classified as atactic [11, 12], stereoblock with segments of

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syndiotactic sequences [7, 13], or predominantly syndiotactic [8]. The lack of agreement results from the fact that the usual methods for determining the stereoregularity of a material do not provide unequivocal results for polyacrylonitrile polymers [11, 14].

The polymer can be prepared by organometallic catalysts which may increase the syndiotactic content [11], and by ionizing irradiation of urea canal complexes of acrylonitrile which may increase the isotactic content [15, 16]. Little work has been published, however, on whether these polymers exhibit more order in the chain direction [15–17] compared to the polymer prepared by free-radical polymerization. Indeed, Chiang [18] cites a number of different preparations of the polymer which have identical infra-red spectra, wide-angle X-ray patterns, and density, yet differ widely in dissolution temperature. The last differences are interpreted as reflecting differences in perfection along the polymer chain [18].

A further indication of the formation of ordered regions is the development of lamellar-like structures when acrylic fibres or films are hot-stretched. Wave-like striations have been observed normal to the stretch direction on replicas of fibres which were drawn at 100°C, etched by a high-frequency discharge of activated oxygen, and examined using transmission electron microscopy [7]. The scale of the structures ranges from 80 to 120 Å, and increases with annealing time or temperature [7, 19]. Similar annealing behaviour has been observed in many semicrystalline polymers. The same acrylic films also exhibit a long period of about 100 Å when examined using small-angle X-ray scattering [7, 19].

When acrylic fibres are heat-treated under oxidative conditions, the small-angle X-ray scattering (SAXS) exhibits a distinct but transient meridional peak [20–22]. Fillery and Goodhew [22] studied a commercial terpolymer, Courtelle, and found that after heat-treatment at 220°C under either oxidative or nominally inert conditions, the position of the SAXS peak corresponded to an apparent long period of about 163 Å; but a fine-denier laboratory-prepared homopolymer did not develop an apparent long period [22]. The peak in the copolymer appeared after heat-treating in air for 0.25 h, attained a maximum in 1.5 h, and was undetectable after 16 h. Treatment in partial vacuum delayed the appearance of the peak until 1.0 h, and it was undetectable after 23 h.

Tyson [21] examined a larger diameter polyacrylonitrile fibre, and found an apparent long period of 80 Å. The apparent long period spacing was independent of heat-treatment atmosphere. Hinrichsen [20] studied a number of commercial fibres and found apparent long periods from 110 to 160 Å, but no development of a SAXS peak from Dralon fibres. Treatment of an oriented, laboratory-prepared homopolymer for 1 h, on the other hand, gave an apparent long period of 125 Å, which was invariant with heat-treatment temperatures between 180 and 250°C. Treatment at higher temperatures resulted in variations in the intensity and position of the SAXS peak.

The origin of the apparent long period seen in these studies is unknown. Tyson suggests a recrystallization on row nucleation centres. Fillery and Goodhew believe that the scattering intensity is influenced by fibre diameter and is controlled by the unreacted core of the fibre. Hinrichsen, an advocate of three-dimensional crystallinity in polyacrylonitrile, suggests (a) that the small-angle peak corresponds to the lamellar spacing observed for polymers annealed near their melting point [7], or (b) that the chemical changes associated with stabilization proceed selectively, either in the more ordered phase or the less-ordered phase, to increase the variation in electron density, and indicates that both processes might be occurring simultaneously.

Although morphological structures which resemble single crystals, spherulites, and lamellae have been observed in polyacrylonitrile, it remains difficult to reconcile them with the lack of order observed in X-ray and electron diffraction patterns and the general lack of stereoregularity of the material. The present paper focuses on the development of periodic density fluctuations along the fibre axis (corresponding to the apparent long period) under conditions of oxidative stabilization. Quantitative data which confirm the phenomenon are presented, and an interpretation is offered which is based in part on the mechanism of stabilization outlined in Part 1 [23].

2. Experimental procedure

2.1. Materials

Two acrylic fibres were employed in this study. Fibre C is a terpolymer containing about 6% methyl acrylate, 1% itaconic acid, and 93% acrylonitrile. It is manufactured by wet-spinning an inorganic salt solution into a bath containing a lower concentration of salt. Fibre M is a co-

polymer containing 93% acrylonitrile and 7% vinyl acetate. It is also wet-spun, but the solvents and spin bath contain organic liquids.

Fibre C was received in the form of crimped tows, with a filament denier of about 3.8 (cross-sectional area $3.6 \times 10^{-6} \text{ cm}^2$). Fibre M was received as a highly drawn, uncrimped tow with a filament denier of 1.2 (area = $1.1 \times 10^{-6} \text{ cm}^2$). These fibres were heat-treated at constant length in a batch process.

2.2. X-ray diffraction

2.2.1. Wide-angle X-ray scattering

Two diffraction techniques were employed. In one, small silica capillaries containing fibre bundles were mounted in a 5.73 cm Debye–Scherrer camera and exposed to Ni-filtered Cu radiation. In the other approximately equal volumes of fibres were subjected to Ni-filtered Cu radiation on a G.E. diffractometer. Intensity scans were made from $2\theta = 12^\circ$ to 20° with a 1° entrance (MR) slit and a 0.2° receiving slit.

2.2.2. Small-angle X-ray scattering

A modified Rigaku–Denke RU3V diffraction unit, which utilizes double pinhole collimators 330 mm apart, a flat-plate camera 300 mm from the specimen, and a rotating anode generator to produce high energy (50 kV, 100 mA) Ni-filtered Cu radiation, was employed to obtain small-angle data. Relative intensities on film were transposed into plots with the use of a microdensitometer. No corrections for absorption, background, or noise were made, but care was exercised to ensure that equal masses of parallel fibres were investigated.

2.3. Transmission electron microscopy

Fibre M was subjected to an ultrasonic treatment in 50 wt % aqueous DMF solution at 85°C for 6 h, after which the fibres were removed, washed in distilled water, and dried in air. This procedure enables the fibres to separate into their component fibrils, which were subsequently coated with a thin layer of aluminium and examined using a JEM transmission electron microscope at 60 to 100 kV. While this treatment is vigorous, it is not expected to introduce spurious structural features.

3. Results and discussion

A transmission electron micrograph of a representative fibril of fibre M is shown in Fig. 1. Because the fibril is a product of the fibrillation treatment on highly drawn fibres, entropic shrinkage occurs when the material is heated by the electron beam during TEM studies. Although the ensuing motion limits the resolution, bands traversing the fibre are evident, indicating a periodic structure along the fibre axis with a scale, or apparent long period, ranging from 80 to 140 Å. The sample fibres had been drawn in boiling water prior to their examination; and the agreement of the apparent structural period found here with that reported by others in PAN annealed at 100°C is quite good [7, 21]. The small-angle X-ray scattering from this fibre further confirms the presence of a structural period along the fibre axis. A very weak maximum at $2\theta = 60 \text{ min}$ ($k = 4\pi \sin \theta / \lambda = 7.1 \times 10^{-2} \text{ \AA}^{-1}$) is found for this material.

The SAXS intensities from fibres C and M heat-treated for various times at 220°C are shown in Fig. 2 as a function of the meridional angle. The

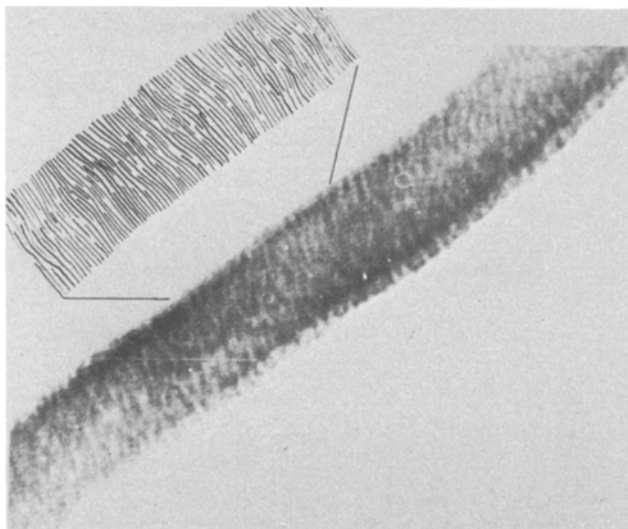


Figure 1 Transmission electron micrograph of a fibril obtained from fibre M.

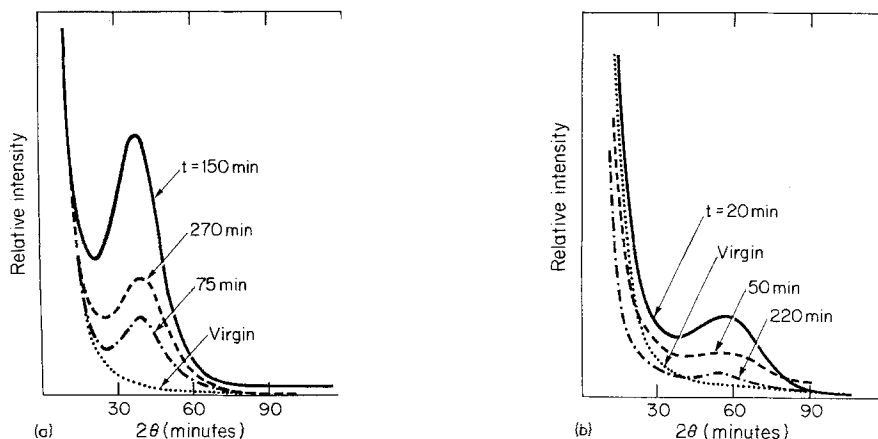


Figure 2 Meridional small-angle X-ray scattering of (a) fibre M, and (b) fibre C, as a function of oxidative stabilization at 220°C. Note that the intensity reaches a maximum at an intermediate time and decreases thereafter. The relative intensities between (a) and (b) are not directly related.

relative intensities of the two plots are not directly comparable as the instrument was rebuilt after the data on fibre C were obtained. A pronounced SAXS peak develops in both fibres after short heat-treatment times, reaches a maximum, decreases, and eventually disappears completely. The maximum is centred at $2\theta = 38$ min for fibre M and $2\theta = 60$ min for fibre C. The heat-treatment time of maximum SAXS intensity is about 150 min for fibre M and about 20 min for fibre C.

To provide a direct comparison of the relative SAXS intensities from the two fibres, successive diffraction runs were carried out on equal quantities of the two fibres heat-treated for times corresponding to the respective maxima in intensity. The results are shown in Fig. 3. As indicated there, the maximum from fibre M corresponds to an ap-

preciably higher intensity of scattering than that from fibre C.

Slade [24] states that the "melting point" of fibres with the composition of fibre M is about 270°C, in accord with the Flory equation for copolymers [25]. This "melting point" is 40°C higher than the heat-treatment temperature used here. The long periods of semicrystalline polymers have been observed to grow measurably with time at similar undercoolings [26], which are above the temperature of initial crystallization. The angular position of the SAXS maximum observed here for both fibre M and fibre C, however, does *not* change with time. This indicates that normal lamellar thickening is not occurring.

All of the oriented acrylic fibres investigated in our laboratory display, in addition to diffuse scattering, two pairs of arcs in the wide angle X-ray pattern. These arcs are indicative of strong molecular orientation along the fibre axis, and correspond to Bragg spacings of 3.03 and 5.27 Å. It has been found, however, that the wide-angle X-ray pattern of fibres thoroughly stabilized in either air or vacuum appears amorphous, showing only a slight degree of orientation. During the oxidative stabilization of fibre M under tension in the range of 220 to 260°C, the wide-angle peaks initially sharpen (i.e. for the initial 30 min at 230°C). Thereafter, the peak intensity decreases with time. After 225 min at 230°C, only a small portion of the original order remains, and stabilization is essentially complete. This behaviour is shown in Fig. 4.

In Part 1 [23], a view of stabilization based on

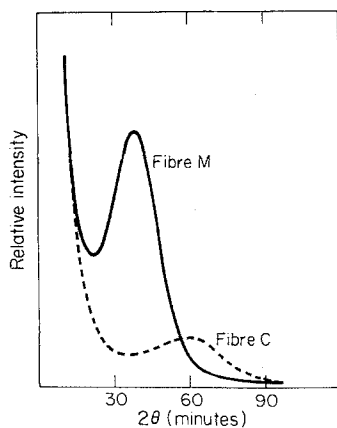


Figure 3 Meridional small-angle X-ray scattering of fibre C and M at maximum intensity of the transient peak.

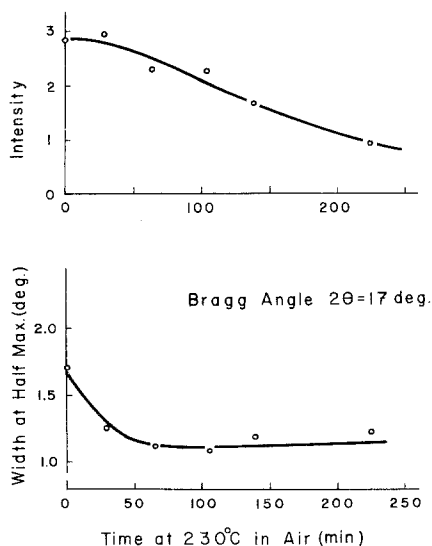


Figure 4 Effect of stabilization time at 230°C on the wide-angle X-ray pattern of fibre M.

a two-step process was discussed. The first step involves all of the reactions, termed “prefatory reactions”, that lead up to and include the polymerization of nitrile groups. The second step consists of all of the reactions that follow nitrile polymerization, which are termed “sequent reactions”. In commercial practice, the sequent reactions include the reaction of oxygen with the products of the prefatory reactions. Further, the stabilization of acrylic fibres shows two different limiting cases: a reaction-limited mechanism, wherein the prefatory reactions proceed slowly throughout the fibre and the sequent reactions follow throughout the fibre; and a diffusion-limited mechanism, wherein the prefatory reactions proceed rapidly throughout the fibre and the sequent reactions are limited by the diffusion of oxygen throughout the previously reacted material. The diffusion-limited case is typified by a two-zone morphology wherein a dark outer mantle is formed during the early stages of thermal treatment, followed by the thickening of the mantle as the core–mantle interface moves toward the centre of the fibre. In contrast, the reaction-limited mechanism is typified by the fibre uniformly darkening throughout its cross-section, without the development of mantle–core zones.

Fibre M stabilizes by the reaction-limited mechanism under the conditions of fibre diameter and temperature employed in this study. One can envision the prefatory reactions occurring in selected regions distributed throughout the fibres – regions

in which the local structure and/or chemistry facilitate enhanced reaction kinetics. The sequent reactions occur thereafter only in those regions in which prefatory reactions have occurred. The peak observed at $2\theta = 38$ min in the SAXS pattern (see Fig. 2a above), reflects structural and /or chemical order in the precursor acrylic fibres, which provides sites of enhanced reactivity spatially distributed with some regularity along the fibre axis. As the reaction proceeds, the reacted regions increase in number (but not much in size) until the selected regions of enhanced reaction rate are used up and the remaining regions begin to transform.

Fibre C on the other hand, exhibits diffusion-limited stabilization kinetics for the temperatures and fibre diameters used in the present study. A peak in the SAXS pattern is observed at about $2\theta = 60$ min. This peak reaches maximum intensity at short times (in the range of 20 min or so). This is about the time when the two-zone morphology is perceived at the given temperature of heat-treatment. Still longer times are required before the outer zone is seen to advance toward the centre of the fibre.

A peak in the SAXS pattern (albeit weaker) is also observed when fibre C is pyrolysed under nominally inert conditions [22]. This indicates that the prefatory reactions contribute to the change in electron density, and hence to the SAXS peak. It should be noted, however, that all precursor fibres contain some dissolved oxygen, and a portion of this can react before most of the sequent reactions occur. On the other hand, fibre shrinkage from the prefatory reactions alone will cause densification of the selected regions of enhanced reactivity.

The time of appearance of the maximum SAXS intensity from fibre C, relative to the time of appearance of the two-zone morphology, may be understood as follows: at short times, prefatory reactions occur throughout the fibre, while sequent reactions occur only in the outer region. The peak observed in the SAXS pattern again reflects sites of enhanced reactivity spatially distributed with some regularity along the fibre axis. Until about the time when the two-zone structure is first perceived, the reacted regions increase in number but remain nearly constant in size. Thereafter, further reactions in the outer zone include transformation in regions of smaller reaction rate, decreasing the differences in electron density in this zone. By the time the outer zone (mantle) begins to move toward the centre of the fibre, the differences in

electron density in the mantle are relatively small; and further sequent reactions take place principally in a rather narrow mantle—core boundary region.

The greater peak intensity from fibre M compared with that from fibre C very likely reflects differences in chemistry (and hence reactivity) between the fibres, and also reflects the greater volume of the fibres in which density differences between reacted and unreacted regions contribute to the SAXS maximum (the entire cross-section for fibre M as opposed to only the mantle region for fibre C). The differences in diffraction angle of the SAXS maxima for the two fibres reflect differences in their chemistry and processing, and concomitant differences in the scale of micro-structure.

The lack of agreement on the morphological structure of polyacrylonitrile fibres described in Section 1 as well as the existence of the transient peak observed during heat-treatment, can be explained with a new model for the texture of oriented acrylic fibres. It is well established that acrylic fibres are composed of fibrils [27–30] of the order of 100 to 1000 Å diameter. These fibrils arise from the coagulation process used in spinning the fibres, wherein fibrillar structures are interspersed with voids prior to collapse of the as-spun gel network. They exist in both wet-spun and dry-spun acrylic fibres [30]. The fibrils are aligned parallel to the fibre axis during the drawing process.

Fig. 5, which depicts the suggested new model,

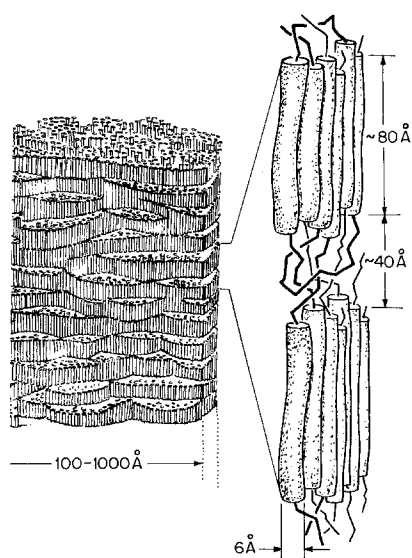


Figure 5 Schematic of molecular structure in highly oriented acrylic fibres.

shows two orders of fine structure within a typical acrylic fibril. The major order consists of rods aligned parallel to the fibril and also the fibre axis. The diameter of the rods is about 6 Å (based on studies with molecular models). The lamellar-like texture is a result of the rods being “ordered” into a liquid crystal-type array perpendicular to the fibrillar axis. The liquid crystal ordering is more or less evenly spaced along the fibril axis, with a repeat spacing of 120 Å consisting of rods approximately 80 Å long interspersed with less ordered material of approximately 40 Å between the rods. Within each rod, the polymer is in a contorted helical shape with the nitrile groups oriented at various angles to the axis of the rod. The rod-like model is similar to that of Bohn *et al.* [1]; but the present model differs from the previous in that here two different textures exist along the fibril axis. The rods are not in perfect alignment with respect to the rod ends, but rather exhibit some misalignment as depicted in the figure. The disordered regions between the layers of aligned rods consist of loops, folds, entanglements, chain ends, defects, co-monomer sequences, tie chains, etc. with a similar lack of order as that expected in the amorphous regions in a three-dimensional semi-crystalline polymer such as polyethylene.

The dimensions chosen for the figure arise from a number of separate observations. A rough calculation of the dimension of the liquid-crystal ordered regions along the length of the fibre can be made by application of the Scherrer line-broadening formula [31] to the wide-angle data. According to this relation, the size of the coherently diffracting array, t , can be expressed:

$$t = 0.9\lambda/\beta \cos \theta, \quad (1)$$

where λ is the wavelength of the incident radiation (1.54 Å), θ is the Bragg angle (8.4°) of the most intense peak, and β is the breadth at half maximum of the measured peak (1.5°). For the present case, t , is estimated as about 55 Å. Since corrections for instrumental broadening and strain have not been made, the value of 55 Å should be taken as an underestimate of the size of diffracting arrays. Considering further the approximations involved in using the Scherrer relation, the size of the arrays should be taken as about 50 to 100 Å. This range agrees quite well with the values derived from Figs. 1 and 2. Application of Bragg's Law to the locations of the peaks in Fig. 2 give values of

139 and 88 Å for fibres M and C respectively. Further examination of Fig. 1, the examination of other electron micrographs, plus many reported estimates of the "crystallinity" of acrylic materials suggests that the long period can be divided into regions of roughly two-thirds "ordered" material and one-third disordered material; hence the assigned values of approximately 80 and 40 Å, respectively.

The wide-angle pattern of oriented acrylic films and fibres exhibits two broad arcs which arise from spacings of roughly 3.0 and 5.3 Å, but the breadth of the arcs is indicative of a distribution which exists about these distances. These same arcs are observed by several authors in the electron diffraction studies. Klement and Geil [2], for example studied platelets of polyacrylonitrile obtained by slow cooling of dilute solutions of polymer in propylene carbonate. These authors have observed many broad diffraction spots in the equatorial direction, but no determinable repeat distance in the chain direction.

Studies made by the present authors with space filling molecular models using the tetrahedral angle of 109° , atomic radii of $C_{\text{single}} = 0.77$, $C_{\text{triple}} = 0.60$, $H = 0.30$, $N_{\text{triple}} = 0.55$ Å and van der Waal's radii of $H = 1.2$, $N = 1.5$ Å have demonstrated that atactic polyacrylonitrile with the nitrile groups arranged for minimum interaction along a chain could only be formed with a close-packed interchain distance of ~ 5.7 Å. Smaller spacings such as 5.3 and 3.0 Å are sterically impossible. It is, therefore, suggested that the rods are roughly circular in cross-section with a diameter of approximately 6 Å, consistent with the given by Holland *et al.* [9] and Bohn *et al.* [1]. The molecular model study also indicated that the nitrile groups could form dipolar pairs with the carbon of one nitrile group juxtaposed with the nitrogen of an adjacent group.

The partially ordered array of acrylic rods may be considered a solid version of a distorted amphiphilic middle phase liquid crystal [32]. Such materials readily assume a spherulitic morphology and, like polyacrylonitrile, are characterized by a negative birefringence [3, 32].

The platelets of polyacrylonitrile which resemble single crystals of crystallizable polymers can be considered as a single lamellae-like array of acrylic rods. This would explain the lack of sharply delineated crystalline edges in the platelets. The thickness dimension of the platelets, then, is

essentially the length of the rods, neglecting the disordered loops at the rod ends.

It is difficult to establish unequivocally the morphology depicted in Fig. 5 as the structure of ordinary acrylic materials because of the extremely small density differences between the ordered and the disordered regions. Chiang [18] and also Krigbaum and Tokota [33] have given evidence for the small density differences based on dilatometric studies. The contrast between the "ordered" and the unordered regions can be enhanced by imparting very high orientation to the materials [19], by an uncatalysed thermal treatment (Fig. 2 and [20–22]), or perhaps by incorporation of metallic salts [34].

4. Conclusions

A substantial body of evidence based on wide and small-angle X-ray diffraction and transmission electron microscopy has been presented which suggests that fluctuations in density associated with alternating "ordered" and disordered regions occur along the length of textile acrylic fibres with a periodicity of 70 to 170 Å. Although PAN prepared by free radical polymerization is essentially atactic, under appropriate conditions it can assume spherulitic or even single crystal-like textures; but no X-ray reflections or electron diffraction spots occur which indicate significant order along the chain axis. For this reason and from stereochemical considerations, it is suggested that the order in atactic acrylic polymers is similar to that in amphiphilic middle-phase liquid crystals. The structure of acrylic fibres, therefore, consists of elongated voids and fibrils: the fibrils are composed of bundles of rods (ordered domains) 50 to 100 Å along the length of the fibre with 30 to 70 Å amorphous regions (disordered domains). Within the ordered domains, the nitrile groups are oriented at a variety of angles to the fibre axis, are interpenetrating between adjacent rods, but tend to repel one another along a given rod.

During the oxidative stabilization of acrylic fibres, a peak in the small-angle X-ray pattern is observed at intermediate times. This peak disappears with prolonged heat-treatment. Wide-angle X-ray data show a continuous decrease in the amount of the ordered domains upon heat-treatment. It is deduced that the mechanism of contrast, giving rise to the peak in SAXS, results from selective degradation of the acrylic structure, a mechanism similar to that proposed by Ruland for cellulose

[35]. It is suggested that both prefatory and sequent reactions contribute to the enhanced contrast in electron density.

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