

AD-A058 639

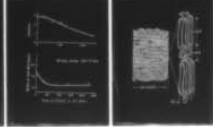
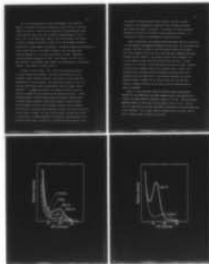
MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF MATERIA--ETC F/6 11/5
OXIDATIVE STABILIZATION OF ACRYLIC FIBERS. II. MORPHOLOGY OF PO--ETC(U)
AUG 78 S B WARNER, L H PEEBLES, D R UHLMANN N00014-75-C-0542

UNCLASSIFIED

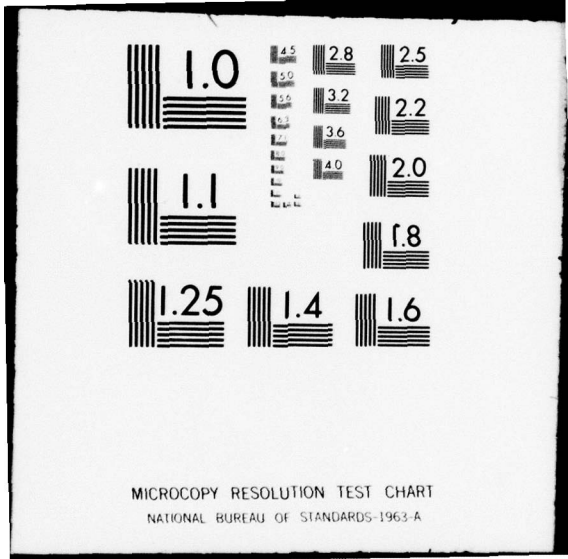
TR-11

NL

| OF |
AD
A058639



END
DATE
FILMED
11-78
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER TECHNICAL REPORT NO. 11 (14) TR-71	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Oxidative Stabilization of Acrylic Fibers. II. Morphology of Polyacrylonitrile.	5. TYPE OF REPORT & PERIOD COVERED 9) Technical Report.	
7. AUTHOR(s) S.B./Warner, L.H./Peebles, Jr., and D.R./Uhlmann	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, Mass. 02139	8. CONTRACT OR GRANT NUMBER(s) Contract No. N00014-75-C-0542	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Street Arlington, VA 22217	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-534	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	12. REPORT DATE 11) August 1978	13. NUMBER OF PAGES
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited	15. SECURITY CLASS. (of this report) 12) 300p	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	DDC RECEIVED SEP 14 1978 LIBRARY BU F	
18. SUPPLEMENTARY NOTES Prepared for submission to the Journal of Materials Science		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polyacrylonitrile X-ray diffraction Crystal structure Small angle X-rays Morphology Wide angle X-rays Liquid Crystals		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new model for the structure of oriented acrylic fibers is presented. The polyacrylonitrile molecules (or the acrylic sequences in a copolymer) 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 6.0A in which the nitrile units are oriented at various angles to the rod axis, but are spaced irregularly on or near the		

AD A0 586396

DDC FILE COPY

LEVEL

409 463

78
555
JMU

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 fibers 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. ↗

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
11	SPECIAL
A	

OFFICE OF NAVAL RESEARCH
Contract N00014-75-C-0542
Task No. 356-534

Technical Report No. 11

OXIDATIVE STABILIZATION OF ACRYLIC FIBERS.
II. MORPHOLOGY OF POLYACRYLONITRILE

by

S.B. Warner, L.H. Peebles, Jr., and D.R. Uhlmann
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

August 1978

Technical Report prepared for publication in Journal of Materials Science
Approved for public release, distribution unlimited

Prepared for

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

ABSTRACT

A new model for the structure of oriented acrylic fibers is presented. The polyacrylonitrile molecules (or the acrylic sequences in a copolymer) 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 6.0Å 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 fibers 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.

I. INTRODUCTION

The structure of polyacrylonitrile and acrylic copolymers 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 Å 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 case, electron diffraction from the platelets shows only reflections of the (h,k,0) 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 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, Chaing (18) cites a number of different preparations of the polymer which have identical infrared 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 fibers or films are hot-stretched. Wave-like striations have been observed normal to the stretch direction on replicas of fibers 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^oA, and increases with annealing time or temperature (7, 19). Similar annealing behavior has been observed in many semi-crystalline polymers. The same acrylic films also exhibit a long period of about 100^oA when examined using small X-ray scattering (7, 19).

When acrylic fibers 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 220C under either oxidative or nominally inert conditions, the position of the SAXS peak corresponded to an apparent long period of about 100Å. By comparison, a commercial homopolymer, Dralon, had an apparent long period of about 163Å; 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 hr., attained a maximum in 1.5 hr., and was undetectable after 16 hrs. Treatment in partial vacuum delayed the appearance of the peak until 1.0 hr., and it was undetectable after 23 hr.

Tyson (21) examined a larger diameter polycrylonitrile fiber, and found an apparent long period of 80Å. The apparent long period spacing was independent of heat treatment atmosphere. Hinrichsen (20) studied a number of commercial fibers and found apparent long periods from 110 to 160Å, but no development of a SAXS peak from Dralon fibers. Treatment of an oriented, laboratory-prepared homopolymer for one hr., on the other hand, gave an apparent long period of 125Å, which was invariant with heat treatment temperatures between 180 and 250C. 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 centers. Fillery and Goodhew believe that the scattering intensity is influenced by fiber diameter and is controlled by the unreacted core of the fiber. Hinrichsen, an advocate of 3-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 fiber 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 Paper I of this series (23).

II. EXPERIMENTAL PROCEDURE

A. Materials

Two acrylic fibers were employed in this study. Fiber C is a terpolymer containing about 6 pct. methyl acrylate, 1 pct. itaconic acid, and 93 pct. acrylonitrile: It is manufactured by wet-spinning an inorganic salt solution into a bath containing a lower concentration of salt. Fiber M is a copolymer containing 93 pct. acrylonitrile and 7 pct. vinyl acetate. It is also wet-spun, but the solvents and spin bath contain organic liquids.

Fiber C was received in the form of crimped tows, with a filament denier of about 3.8 (cross-sectional area: $3.6 \times 10^{-6} \text{ cm}^2$). Fiber 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 fibers were heat treated at constant length in a batch process.

B. X-Ray Diffraction

Wide Angle X-Ray Scattering

Two diffraction techniques were employed. In one, small silica capillaries containing fiber 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 fibers 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.

Small Angle X-Ray Scattering

7.

A modified Rigaku-Denki 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 fibers were investigated.

C. Transmission Electron Microscopy

Fiber M was subjected to an ultrasonic treatment in 50 wt. pct. aqueous DMF solution at 85C for 6 hrs., after which the fibers were removed, washed in distilled water, and dried in air. This procedure enables the fibers to separate into their component fibrils, which were subsequently coated with a thin layer of aluminum and examined using a JEM transmission electron microscope at 60-100 kv.

III. RESULTS AND DISCUSSION

A transmission electron micrograph of a representative fibril of fiber M is shown in Fig. 1. Because the fibril is a product of the fibrillation treatment on highly drawn fibers, 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 fiber are evident, indicating a periodic structure along

the fiber axis with a scale, or apparent long period, ranging from 80 to 140^oA. The sample fibers 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 100C is quite good (7, 21). The small angle X-ray scattering from this fiber further confirms the presence of a structural period along the fiber axis. A very weak maximum at $2\theta=30$ min. ($k = \frac{4\pi \sin \theta}{\lambda} = 3.6 \times 10^{-2} \text{ \AA}^{-1}$) is found for this material.

The SAXS intensities from fibers C & M heat treated for various times at 220 C are shown in Fig. 2 as a function of the meridional angle. The relative intensities of the two plots are not directly comparable as the instrument was rebuilt after the data on fiber C were obtained. A pronounced SAXS peak develops in both fibers after short heat treatment times, reaches a maximum, decreases, and eventually disappears completely. The maximum is centered at $2\theta=19$ min for fiber M and $2\theta=30$ min for fiber C. The heat treatment time of maximum SAXS intensity is about 150 min. for fiber M and about 20 min. for fiber C.

To provide a direct comparison of the relative SAXS intensities from the two fibers, successive diffraction runs were carried out on equal quantities of the two fibers heat treated for times corresponding to the respective maxima in intensity. The results are shown in Fig. 3. As indicated there, the maximum from fiber M corresponds to an appreciably higher intensity of scattering than that from fiber C.

Slade (24) states that the "melting point" of fibers with the composition of fiber M is about 270C, 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 fiber M and fiber C however, does not change with time. This indicates that normal lamellar thickening is not occurring.

All of the oriented acrylic fibers 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 fiber axis, and correspond to Bragg spacings of 3.03 \AA and 5.27 \AA . It has been found, however, that the wide angle X-ray pattern of fibers thoroughly stabilized in either air or vacuum appears amorphous, showing only a slight degree of orientation. During the oxidative stabilization of fiber M under tension in the range of 220-260 C, the wide angle peaks initially sharpen (i.e., for the initial 30 min. at 230C). 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 behavior is shown in Fig. 4.

In Paper I of this series (23), a view of stabilization based on a two-step process was discussed. The first step involves all of the reactions, terms "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 fibers shows two different limiting cases: a reaction-limited mechanism, wherein the prefatory reactions proceed slowly throughout the fiber and the sequent reactions follow throughout the fiber; and a diffusion-limited mechanism, wherein the prefatory reactions proceed rapidly throughout the fiber 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 center of the fiber. In contrast, the reaction-limited mechanism is typified by the fiber uniformly darkening throughout its cross-section, without the development of mantle-core zones.

Fiber M stabilizes by the reaction-limited mechanism under the conditions of fiber diameter and temperature employed in this study. One can envision the prefatory reactions occurring in selected regions distributed throughout the fibers--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 $t = 19$ min. in the SAXS pattern (see Fig. 2a above), reflects structural and/or chemical order in the precursor acrylic fibers, which provides sites of enhanced reactivity spatially distributed with some regularity along the fiber 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.

Fiber C on the other hand, exhibits diffusion-limited stabilization kinetics for the temperatures and fiber diameters used in the present study. A peak in the SAXS pattern is observed at about $t = 30$ 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 center of the fiber.

A peak in the SAXS pattern (albeit weaker) is also observed when fiber C is pyrolyzed 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 fibers contain some dissolved oxygen, and a portion of this can react before most of the sequent reactions occur. On the other hand, fiber 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 fiber 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 fiber, 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 fiber 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 when the outer zone (mantle) begins to move toward the center of the fiber, 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 fiber M compared with that from fiber C very likely reflects differences in chemistry--and hence reactivity--between the fibers, and also reflects the greater volume of the fibers in which density differences between reacted and unreacted regions contribute to the SAXS maximum (the entire cross section for fiber M vs only the mantle region for fiber C).

The differences in diffraction angle of the SAXS maxima for the two fibers reflect differences in their chemistry and processing, and concomitant differences in the scale of microstructure.

The lack of agreement on the morphological structure of polyacrylonitrile fibers described in the Introduction 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 fibers. It is well established that acrylic fibers are composed of fibrils (27-30) of the order of 100-1000 \AA in diameter. These fibrils arise from the coagulation process used in spinning the fibers, 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 fibers (30). The fibrils are aligned parallel to the fiber axis during the drawing process.

Fig. 5, which depicts the suggested new model, 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 fiber axis. The diameter of the rods is about 6 \AA (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 \AA consisting of rods approximately 80 \AA long interspersed with less ordered material of approximately 40 \AA 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, comonomer sequences, tie chains, etc. with a similar lack of order as that expected in the amorphous regions in a 3-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 fiber 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 the diffracting arrays. Considering further the approximations involved in using the Scherrer relation, the size of the arrays should be taken as about 50-100 Å. This range agrees quite well with the values derived from

Figs. 1 and 2. Application of Braggs Law to the locations of the peaks in Fig. 2 give values of 139 and 88 Å for fibers 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 2/3 "ordered" material and 1/3 disordered material; hence the assigned values of approximately 80 and 40 Å respectively.

The wide angle pattern of oriented acrylic films and fibers 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 exists about these distances. These same arcs are observed by several authors in the electron diffraction studies. Klement and Geil (2), e.g., 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 spacings 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 Tokota and Krigbarum (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 uncatalyzed thermal treatment (Fig. 2 and Refs. 20-22), or perhaps by incorporation of metallic salts (34).

IV. CONCLUSIONS

A substantial body of evidence based on wide angle 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 fibers with a periodicity of 70-170 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 lyotropic amohiphilic middle phase liquid crystals. The structure of acrylic fibers, therefore, consists of elongated voids and fibrils: The fibrils are composed of bundles of rods (ordered domains) 50-100 Å long, containing the irregularly coiling molecules. These bundles of rods alternate along the length of the fiber with 30-70 Å amorphous regions (disordered domains). Within the ordered domains, the nitrile groups are oriented at a variety of angles to the fiber axis, are interpenetrating between adjacent rods, but tend to repel one another along a given rod.

During the oxidative stabilization of acrylic fibers, 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.

ACKNOWLEDGEMENTS

Financial support for the present work was provided by the Office of Naval Research. This support is gratefully acknowledged.

REFERENCES

1. Bohn, C.R., Schaeffgen, J.R., and Statton, W.O., J. Polym. Sci., 55 (1961) 531.
2. Klement, J., and Geil, P., J. Polym. Sci. Part A-2, 6 (1968) 1381.
3. Holland, V.F., J. Polym. Sci., 43 (1960) 572.
4. Statton, W.O., Ann. N.Y. Acad. Sci., 83 (1959) 27.
5. Lindenmeyer, P.H., and Hosemann, R., J. Appl. Phys., 34 (1963) 42.
6. Urbanczyk, G.W., Zeszyty Nauk. Polytech. Lodz, Wlokiennictwo 9 (1962) 79; through Chem. Abstr. 61 (1964) 5836b.
7. Hinrichsen, G. and Orth, H., Koll. Z. u. Z. Polym., 247 (1971) 844.
8. Stefani, R., Chevreton, M., Garnier, M., and Eyraud, C., Compt. Rend. 251 (1960) 2174.
9. Holland, V.F., Mitchell, S.B., Hunter, W.L., and Lindenmeyer, P.H., J. Polym. Sci., 62 (1962) 145.
10. Kast, W., in Landolt-Bornstein Tabellen, Vol. 4, 6th Edition, Part 3 Springer Verlag, Berlin, 1957, p. 1050.
11. Schaefer, J., Macromolecules, 4 (1971) 105.
12. Liang, C.Y., and Krimm, S., J. Polym. Sci., 31 (1958) 513.
13. Huang, Y.S., and Koenig, J.L., J. Appl. Spectroscopy, 25 (1967) 620.
14. Colvin, B.G., and Storr, P., Europ. Polym. J., 10 (1974) 337.
15. White, D.M., J. Am. Chem. Soc., 82 (1960) 5678.
16. Kawasaki, M., Maekawa, T., Hayashi, K., and Okamura, S., J. Macromol. Chem., 1 (1966) 489.
17. Chiang, R., Rhodes, J.H., and Holland, V.F., J. Polym. Sci., Part A, 3 (1965) 479.
18. Chiang, R., J. Polym. Sci., Part A, 1 (1963) 2765.
19. Hinrichsen, G., and Orth, H., J. Polym. Sci., Part B. 9 (1971) 529.

20. Hinrichsen, G., J. Appl. Polym. Sci., 17 (1973) 3305.
21. Tyson, C.N., Nature Physical Science 229 (1971) 121.
22. Fillery, M.E., and Goodhew, P.J., Nature Physical Science 233 (1971) 118.
23. Warner, S.B., Peebles, L.H., and Uhlmann, D.R., J. Materials Sci., 00 (1978) 0000. Part. I.
24. Slade, P.E., Thermochim. Acta, 1 (1970) 459.
25. Flory, P.J. Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N.Y., 1953.
26. Fischer, E., and Schmidt, G., Angew. Chem., Int. Ed., 1 (1972) 488.
27. Johnson, D.J., and Tyson, C.N., Brit. J. Appl. Phys., (J. Phys., D) Ser. 2, 2 (1969) 787.
28. Watt, W. and Johnson, W., Appl. Polym. Symp. 9 (1969) 215.
29. Tucker, P., and George, W., Polym. Eng. & Sci., 12 (1972) 364.
30. Craig, J.P., Knudsen, J.P., and Holland, V.F., Textile Res. J., 32 (1962) 435.
31. Cullity, B.D., Elements of X-ray Diffraction, Addison Wesley, 1956, Chapter 3.
32. Gray, G.W., and Winsor, P.A. (eds.), Liquid Crystals and Plastic Crystals, Vol. 2, Halsted Press 1975.
33. Krigbaum, W.R., and Tokita, N.J., J. Polym. Sci., 43 (1960) 467.
34. Moutaud, G.N., and Cauville, R.J., Proc. 3rd Carbon Conf. Ind. Carbon and Graphite, London, 1970, p. 475.
35. Ruland, W., J. Polym. Sci., Part C 28 (1969) 141.

FIGURE CAPTIONS

Fig. 1 - Transition electron micrograph of a fibril obtained from Fiber M.

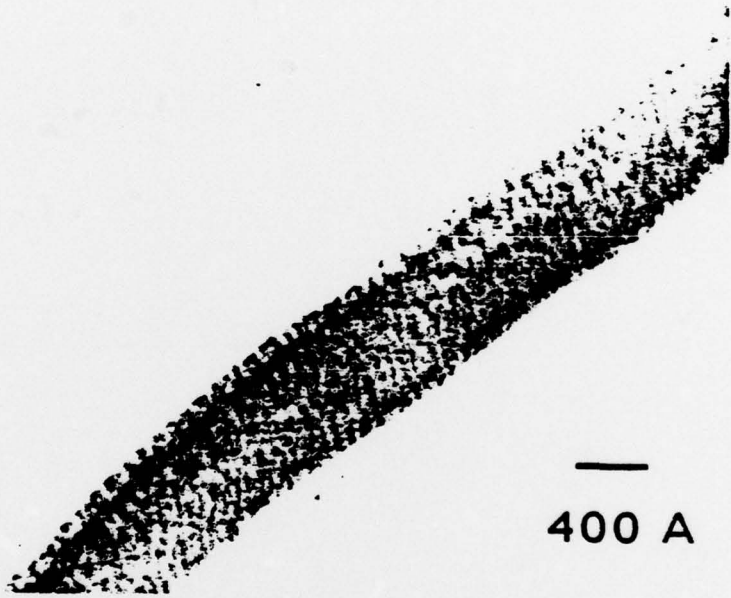
Fig. 2 - Meridional small angle X-ray scattering of (a) fiber M and
(b) fiber C as a function of oxidative stabilization at 220°.

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.

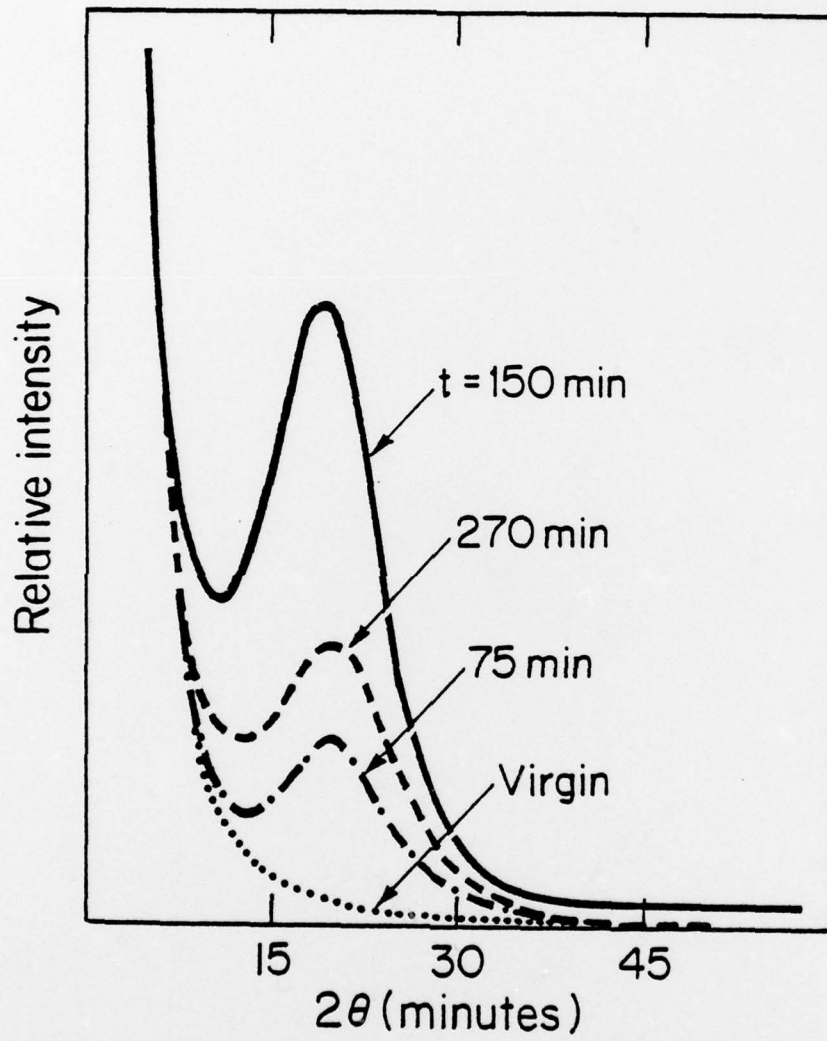
Fig. 3 - Meridional small angle X-ray scattering of fibers C and M at maximum intensity of the transient peak.

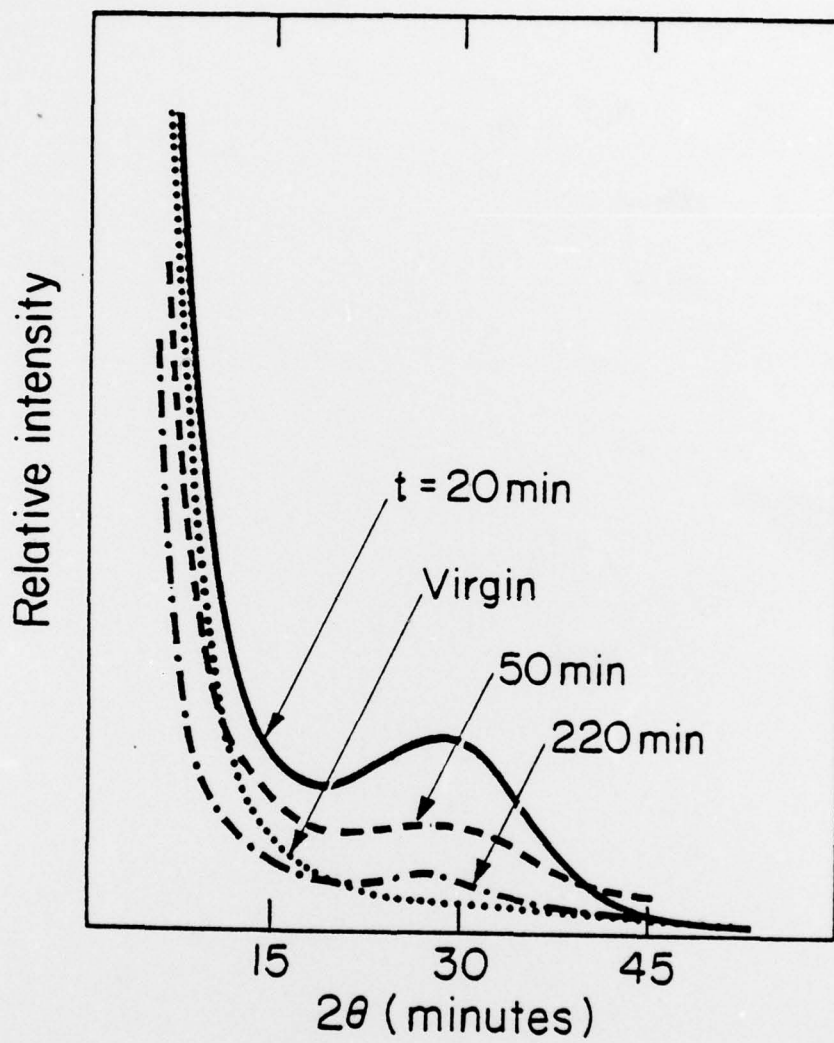
Fig. 4 - Effect of stabilization time at 230 C on the wide angle X-ray pattern of Fiber M.

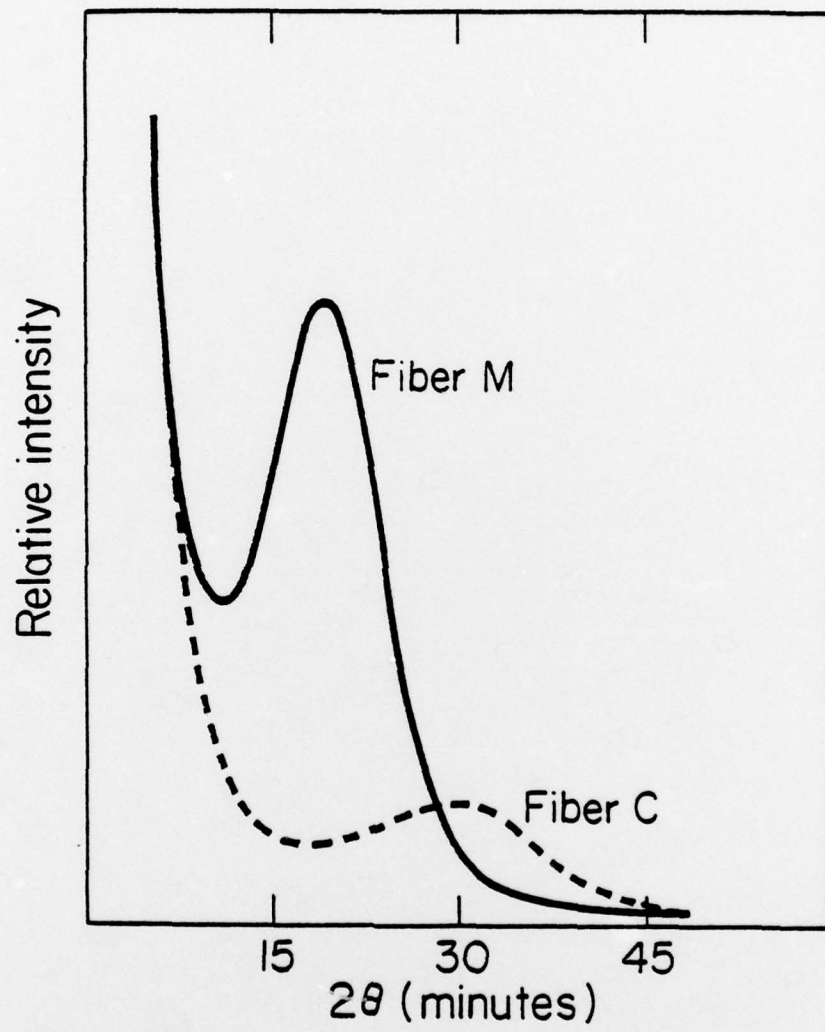
Fig. 5 - Schematic of molecular structure in highly oriented acrylic fibers.

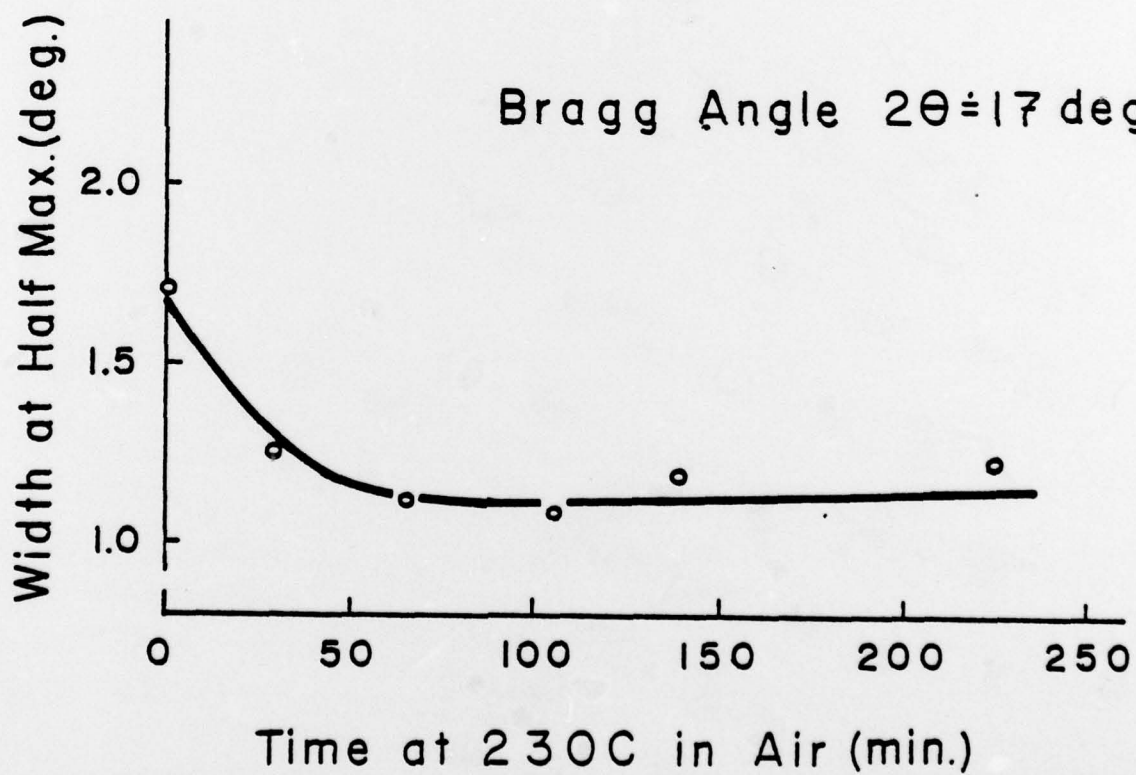
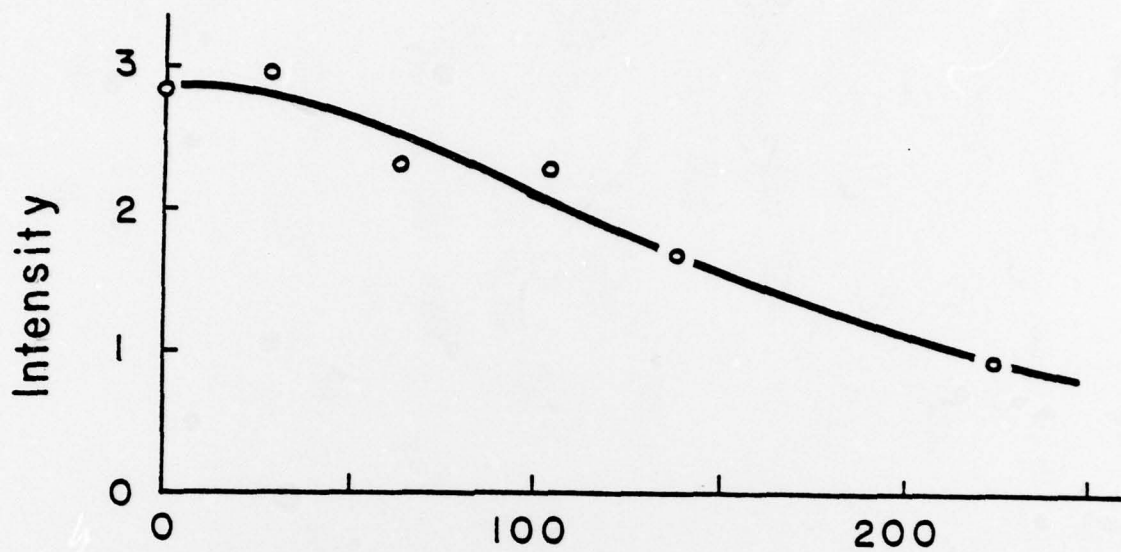


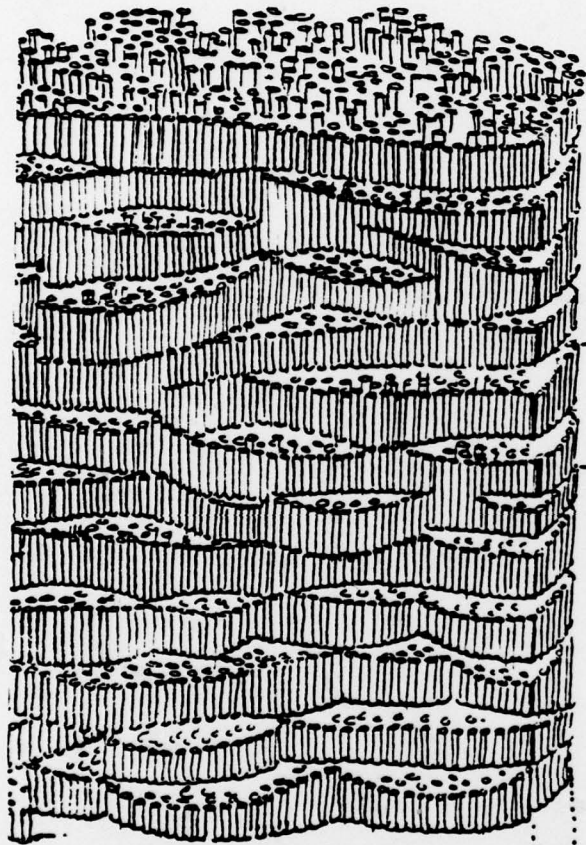
—
400 A











100-1000 Å

