

On the Origin of Order-Disorder in Drawn Polyacrylonitrile

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Synopsis

Drawn polyacrylonitrile can be characterized only insufficiently with regard to its molecular and supermolecular structures which substantially determine the physical properties. This paper points out that the so-called "superstructure" of polyacrylonitrile fibers can be cleared up after suitable thermooxidative treatment using x-ray small-angle scattering technique. The chemical reactions during the thermo-oxidative treatment lead to a "self-contrasting" effect so that the fibers as such are severely damaged yet information about the supermolecular structure can be obtained. The investigations show that changes in the course of fiber production (spinning, drawing, and annealing processes) affect alterations of the superstructure. The described method of investigation represents a so far unknown possibility for the purpose of detecting the supermolecular structure of drawn polyacrylonitrile.

INTRODUCTION

Since the development of carbon fibers with excellent technological properties from polyacrylonitrile precursor fibers, the scientific investigations of the latter have once more become intensified. The thermally initiated degradation processes, which lead to heavy discoloration of the polyacrylonitrile fibers, are of exceptional interest. In addition, some investigations were carried out recently dealing with the origin of supermolecular structure, especially of drawn polyacrylonitrile. Studies on superstructure, e.g., with x-ray wide- and small-angle scattering, yield less information with polyacrylonitrile than with other semicrystalline high polymers. On x-ray wide-angle diagrams of drawn polyacrylonitrile only one intensive and some weak equatorial reflections as well as a few diffuse meridional and layer-line interferences are visible. The absence of more reflections has been looked upon as being an indication that the lateral order of the chain molecules is imperfect and that their alignment and orientation are poor. For this reason polyacrylonitrile has been characterized as a single phasic paracrystal with rodlike structure.¹

By means of electron-microscopic observations and x-ray measurements carried out in the last year, we succeeded in detecting a lamellar colloidal structure of more and less ordered regions in the magnitude of 100 Å. Within the "crystalline" regions, there is a three-dimensional but disturbed

chain arrangement.²⁻⁴ Meanwhile, two more papers were published dealing with the origin of a supermolecular order after heat treatment of fibers at temperatures between 200° and 300°C, a treatment which is applied during carbon fiber production.^{5,6} These studies served as motive for carrying out x-ray small-angle investigations on heat-treated polyacrylonitrile fibers of our own and of commercial origin.

EXPERIMENTAL

Material. The following testing materials were available: (a) Dralon-T-fiber (a polyacrylonitrile homopolymer); (b) Dralon-N-fiber (a copolymer with more than 90% acrylonitrile); (c) Dralon N, undrawn fiber; (d) Orlon 42; (e) Orlon 44; (f) Dolan; (g) Leacryl; (h) Crylor; (i) Melana.

From the initial undrawn Dralon N, fibers were prepared with different draw ratios between 1:3 and 1:7; the draw temperature was increased from 75° to 175°C (high stretching velocity). From the same undrawn material, fibers were drawn by a small hand-stretching machine (slow stretching velocity) to a draw ratio between 1:2 and 1:10 (draw temperature 85°C).

Thermal Treatment. Most of the fiber tows were wound around a rigid frame and heat treated in an air-circulating oven. After the heat treatment, the fibers showed a discoloration from dark brown to deep black. Some heat treatments were carried out under varying annealing temperatures, others with varying annealing times.

Elemental Analysis. From selected samples the content of carbon, nitrogen, oxygen, and hydrogen was determined by the well-known methods of elemental analysis.

Infrared Spectroscopy. The infrared spectra were recorded by a lattice spectrometer, Perkin Elmer Model 421 (Perkin Elmer Corp.).

X-Ray Wide- and Small-Angle Scattering. Photographic wide-angle diagrams were made by commercial flat cameras. For x-ray small-angle measurements we used a Kiessig camera with a spot-like primary beam; the exposure time was 24 hr. Comparison of the scattering intensity of the Kiessig diagrams is somewhat problematic. Care was taken that the same fiber quantity was inserted into the sample holder. Nevertheless, uniform layer thickness on the spot of the incident beam cannot be guaranteed since the fibers, due to several reasons, have a different volume requirement.

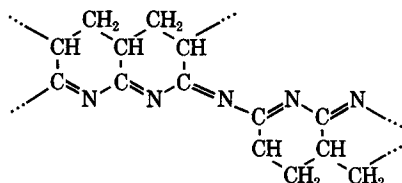
RESULTS AND DISCUSSION

Short Description of Thermo-Oxidative Degradation of Polyacrylonitrile

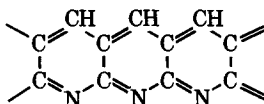
Upon thermal treatment of polyacrylonitrile fibers at temperatures above 170°–180°C, discoloration from light yellow to deep black was observed depending on annealing temperature and time. The color changes are related to an exothermic reaction within the temperature interval of 180° to 380°C, which can be detected, e.g., by differential thermal analysis.⁷⁻¹¹ Under careful experimental conditions the melting

of polyacrylonitrile fibers can be observed (melting point 320°C).¹⁰⁻¹² At the exothermic reaction stage, gaseous products such as HCN, NH₃, nitriles, and so on, are produced. Chemical investigations on discoloration and thermo-oxidative degradation have been published in numerous papers during the last years.¹³⁻³⁸

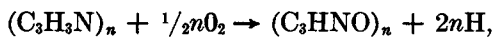
Four recent papers shall be outlined here leading to various reaction mechanisms and different structure models with regard to the heat-treated polyacrylonitrile. Fitzer and Mueller³⁹ suggest that after a preceding initiation, inter- and intramolecular additive reactions between adjacent nitrile groups take place, which result in cyclization of polyacrylonitrile; thus unstable annulated tetrahydronaphthyridine ring systems are formed. By dehydrogenation these systems stabilize into condensed pyridine ring systems and become polymers with an angular ladder structure, as shown below:



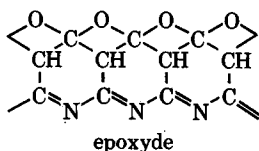
By means of infrared spectroscopic and ESR measurements, Ulbricht and Makschin⁴⁰ investigated the dehydrogenation reaction of polyacrylonitrile. These authors attributed the discoloration in the presence of oxygen mainly to the oxidative dehydrogenation of the thermally cyclized polymers and suggested the following ring system:



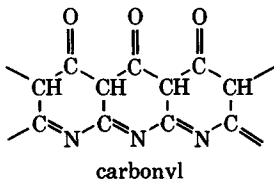
Standage and Matkowski⁴¹ investigated Dralon T; they explained the influence of oxygen in a different way and, using the equation



they came to two possible structure forms:

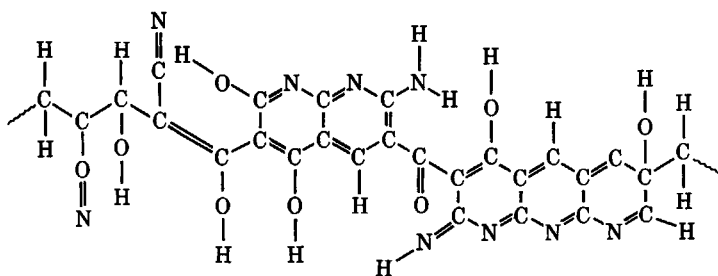


or



Under complete oxidation of polyacrylonitrile, using the equation mentioned above, one has to expect the following percentage by weight: C, 53.7%; H, 1.50%; N, 20.9%; O, 23.9%. The calculated values agreed very well with the experimental results of Standage and Matkowsky.⁴¹

With the aid of infrared spectroscopic measurements on oxidized fibers (Courtelle), Bailey and Clarke⁴² detected the following bonds: C=C; C=N; C—N; O—H; N—H; CH₂; C≡N; and C=O, at which the intensity of the CH₂—, —C≡N, and C=O bonds is reduced. Bailey and Clarke proposed the following structure model for partially oxidized fibers.



The existence of a strong absorption of the NH groups leads to the conclusion that the sequence length of the cyclized rings will be short and probably of different lengths. The cyclized rings do not possess a planar configuration, a result which is in accordance with the suggestions of Fitzer and Mueller³⁹ as mentioned above.

Elemental analysis was carried out in our laboratory on polyacrylonitrile fibers (Dralon N) drawn 1:4 in boiling water. The percentage changes by weight of hydrogen, oxygen, nitrogen, and carbon in relation to annealing temperature at heat treatment periods of 1 hr are plotted in Figure 1. While discolorations are already observed with heat treatment at 180°C, increase in oxygen content and decrease in hydrogen, nitrogen, and carbon contents can only be obtained at about 230°C. This result indicates that the very first discoloration (formation of chromophors) may be produced by the existence of heterocycles. The percentage decrease in carbon and nitrogen is mainly caused by the increase in oxygen, whereas the percentage decrease in hydrogen is connected with a loss of absolute hydrogen content. Some possible reaction mechanisms accounting for the diminution in hydrogen are included in the publications cited above. Figure 1 shows that the untreated sample contains about 3% oxygen; it is well known that Dralon N is a copolymer of acrylonitrile and methylacrylate. With Dralon T (acrylonitrile homopolymer), Standage and Matkowsky⁴¹ indeed obtained less than 1% oxygen for untreated fibers. The elemental analysis and likewise the results of IR measurements demonstrate that an absorption of oxygen takes place at annealing temperatures above 230°C. Oxidation reactions are discussed in the papers of Standage and Matkowsky⁴¹ and Bailey and Clarke.⁴²

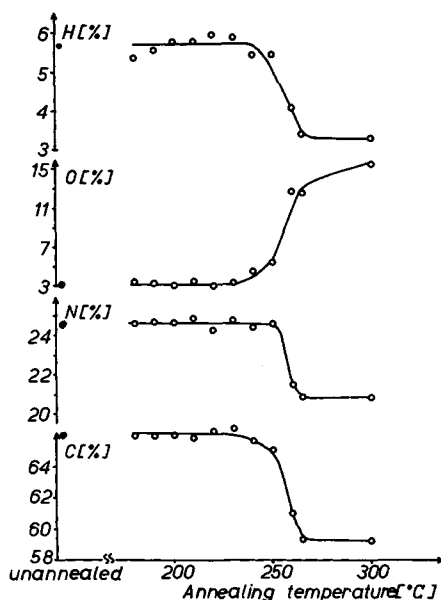


Fig. 1. Hydrogen, oxygen, nitrogen, and carbon content of heat-treated polyacrylonitrile fibers (Dralon N). Annealing time 1 hr.

Investigations of Structure on Unannealed Drawn Polyacrylonitrile

As already mentioned in the introduction, the significance of x-ray measurements on polyacrylonitrile is low because, on the wide-angle diagrams, a comparatively small number of interferences are observed and, on small-angle diagrams of drawn samples, no long-period maxima can be observed. These and additional results of other measuring methods lead many authors to the opinion that polyacrylonitrile is either amorphous^{43,44} or nematic,^{45,46} or two-dimensionally ordered.^{47,48} Lindenmeyer and Hosemann¹ regarded polyacrylonitrile as a paracrystal. On the other hand, there are innumerable indications for a more than two-dimensional order within the polymer. The attempt has been made by some authors to describe a three-dimensional order using a crystal lattice,^{3,49-55} This direction has been confirmed by observations that it is possible to grow spherulites^{46,56} from concentrated solutions or to precipitate lamellar single crystals from dilute solutions.^{3,54,60-62}

By x-ray investigations we were able to find direct evidence of the partially crystalline character of polyacrylonitrile.³ This polymer crystallizes with a strongly disturbed orthorhombic lattice with lattice constants of $a = 10.6 \text{ \AA}$, $b = 11.6 \text{ \AA}$, and $c = 5.04 \text{ \AA}$. In addition to the reflections described by other authors, a few meridional and layer-line reflections could be observed, indicating a position correlation of the chain molecules perpendicular to the molecules. The measured periodicity in chain direction of 5.04 \AA is effected by a zigzag conformation of the syndiotactic chain sequences. Up to now the existence of longer syndiotactic sequences

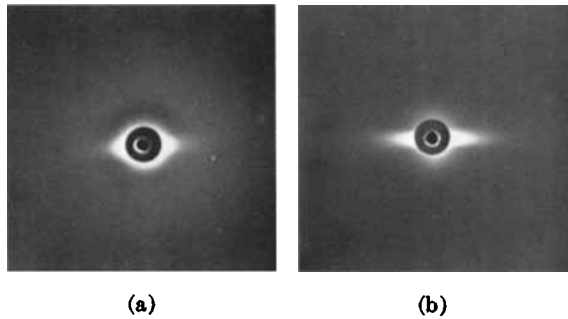


Fig. 2. X-Ray small-angle diagrams of unannealed polyacrylonitrile fibers: (a) Dralon N; (b) Dralon T.

has been doubted. By comparing of NMR, infrared, and Raman spectra, Huang and Koenig⁶³ have recently shown that within polyacrylonitrile there are longer sequences of syndiotactic conformations interrupted by single isotactic or short sequences of isotactic or atactic positions. X-ray small-angle diagrams of unannealed drawn polyacrylonitrile fibers are reproduced in Figure 2 (Dralon N, Dralon T). In addition to an intensive equatorial scattering, a continuous decrease of meridional small-angle scattering is observed. The equatorial scattering may be due to vacuoles within the fiber. A quantitative analysis of equatorial small-angle scattering⁶⁴ is given by Ruscher and Walenta.⁶⁵ The shape and intensity of x-ray small angle patterns depend on spinning and drawing processes and on heat treatment of the fibers. With hot-drawn polyacrylonitrile films, we recently succeeded in finding discrete intensity maxima on the meridian which could be attributed to a colloidal structure with a periodicity of about 100 Å. Convincing optical evidence of a two-phase structure has been furnished by electron micrographs showing a lamellar superstructure.³

Two recent publications, of Tyson⁵ and Fillery and Goodhew,⁶ deal with x-ray small-angle investigations on heat-treated polyacrylonitrile fibers which show distinct meridional maxima. Tyson⁵ maintains that the development of the two-phase structure depends on the thermo-oxidative degradation of polyacrylonitrile. In order to furnish proof that, in the case of the films investigated by us, thermal degradation during the production (dissolving of polymeride, drying and drawing processes of films) is not responsible for the origin of a two-phase-structure polymeride, undrawn and drawn cast films have been investigated by infrared-spectroscopic, ultraviolet-spectroscopic, and viscosimetric measurements. Infrared spectra of polymeride, of unannealed drawn film, and of two undrawn films heat treated at 240°C are given in Figure 3. Prior to the discussion of the infrared spectra, it should be mentioned that the hot-drawn films were fully transparent. According to our experience, the discoloration of polyacrylonitrile films is the most sensitive indication for thermo-oxidative damage. Films and fibers possessing a yellow tinge can hardly be distinguished from untreated specimens by infrared spectroscopy.

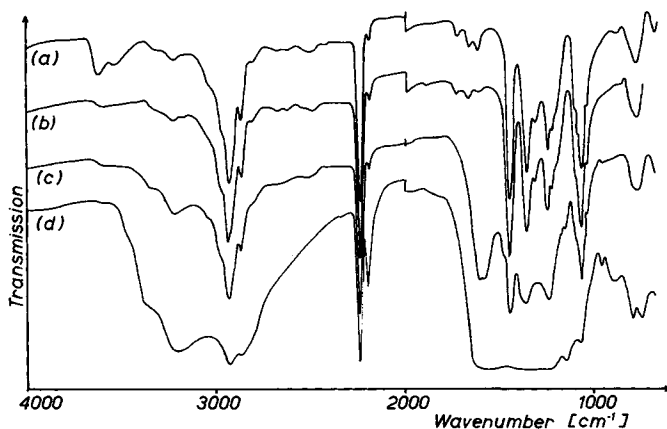


Fig. 3. Infrared spectra of polyacrylonitrile samples: (a) polymeride; (b) film 1:4 drawn at 120°C; (c) film annealed in air for 15 min at 240°C; (d) film annealed in air for 60 min at 240°C.

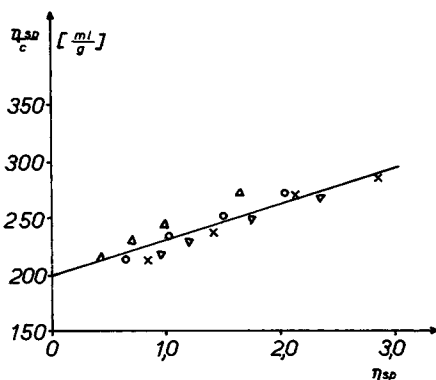


Fig. 4. Measurements of viscosity of various polyacrylonitrile samples: (X) polymeride; (O) solution; (∇) undrawn film; (Δ) drawn film.

Figure 3 shows that the spectra of the films annealed at 240°C, especially in the interval from 1200 to 1800 cm^{-1} , differ substantially from the other spectra.

The infrared spectra of polymeride and drawn film coincide very well; the small bands at 1620 cm^{-1} , correlated with that at 3625/3540 cm^{-1} , are explained by a low concentration of water; the band at 1665 cm^{-1} , by residual DMF; and the band at 1725 cm^{-1} , by C=O bonds of which a small number is always present in polyacrylonitrile.

Further support for our suggestion that the drawn films have not undergone molecular decomposition or crosslinking was taken from viscosimetric measurements. In Figure 4, the quantity η_{sp}/c has been plotted as a function of η_{sp} for polymeride, concentrated solution, and undrawn and drawn films. All points in Figure 4 fit satisfactorily a straight line, i.e., by means of viscosimetric measurements, too, it is impossible to make a distinction

between polymeride and hot-drawn films. On the other hand, polymeride annealed for 1 hr at 220°C possesses a twofold viscosity which moreover remains inconstant during the testing period.

According to these results, it is shown that long-period maxima attributed to a periodical structure of regions of different electron density can be obtained with drawn specimen which have not been submitted to heat treatment connected with any chemical alteration. In the next section, an account is given of thermal treatment which promotes the creation of a two-phase structure due to cyclization and oxidation of polyacrylonitrile.

Investigations of Structure on Oxidized Drawn Polyacrylonitrile

During the production of carbon fibers, the rayon or synthetic precursor fibers are thermo-oxidatively heat treated at temperatures between 200° and 300°C before the final carbonization. Fibers annealed in this way were investigated by means of x-ray small-angle scattering by Tyson⁵ and Fillery and Goodhew.⁶ Both authors observed scattering reflections on the small-angle diagrams of the thermally treated fibers, their shape, distance, and intensities depending on annealing temperature and time. Tyson⁵ suggested a refolding of molecules during the annealing which leads to "nucleation." Fillery and Goodhew⁶ took the view that the scattering intensity is connected with the inner surface of the partially oxidized fibers because they observed differences in the scattering diagrams of fibers with smaller or greater diameter. Moreover, Fillery and Goodhew⁶ suggest that the original condition of the fibers given by draw ratio and diameter would be the determining factor for the molecular rearrangement.

The results of our x-ray investigations on heat treated polyacrylonitrile fibers are arranged in the photographs of Figures 5 to 10. First of all, we were interested in the dependence of small-angle scattering on annealing temperature (see Fig. 5). The intensity of the long-period reflection increases with annealing time and reaches its maximum at 240° to 250°C (annealing time 1 hr). This temperature region coincides fully with that

TABLE I
Radial and Angular Half-Width and Bragg Angle of the Meridional
Main Reflection of Annealed Polyacrylonitrile Fibers^a

Annealing temp., °C	Bragg angle, degrees	Radial half-width, degrees	Angular half-width, degrees
Unannealed	8.65	1.00	16.4
180	8.60	0.88	15.2
190	8.60	0.85	15.4
200	8.60	0.85	15.7
210	8.58	0.85	15.9
220	8.55	0.83	16.7
230	8.58	0.85	15.9
240	8.58	0.83	16.4
250	8.60	0.83	15.2

^a Annealing time 1 hr.

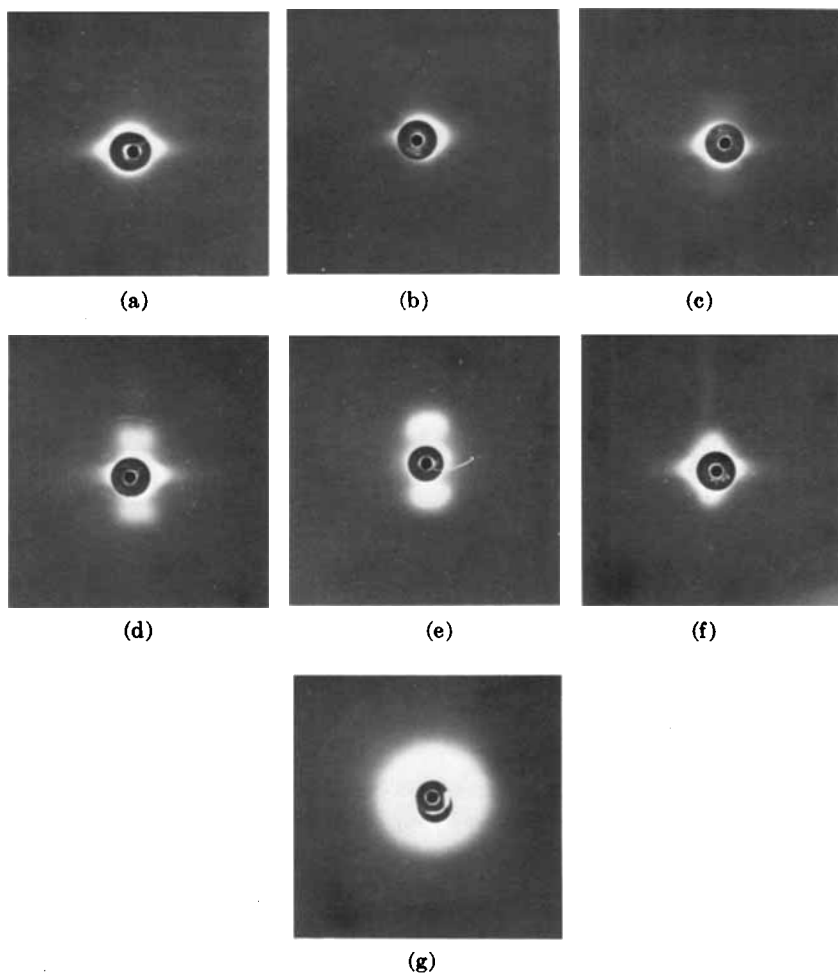


Fig. 5. X-Ray small-angle diagrams of heat-treated polyacrylonitrile fibers. Influence of annealing temperature (annealing time 1 hr): (a) 200°C; (b) 220°C; (c) 230°C; (d) 240°C; (e) 250°C; (f) 260°C; (g) 300°C.

obtained by Tyson.⁵ The small-angle diagrams show a weakly marked four-point character, the intensity maxima lying very close to the small-angle meridian. The long-period value calculated from the distance of the reflections amounts to about 125 Å; as far as one can judge in spite of to the diffusiveness of the reflections, the long period remains constant up to an annealing temperature of 250°C. At higher annealing temperatures, the long-period reflections change both position and intensity; after heat treatment of the fibers at 300°C, an intensive scattering is observed which decreases continuously with scattering angle. By means of x-ray wide-angle measurements, it is impossible to detect significant differences between the specimens annealed at various temperatures. Table I contains

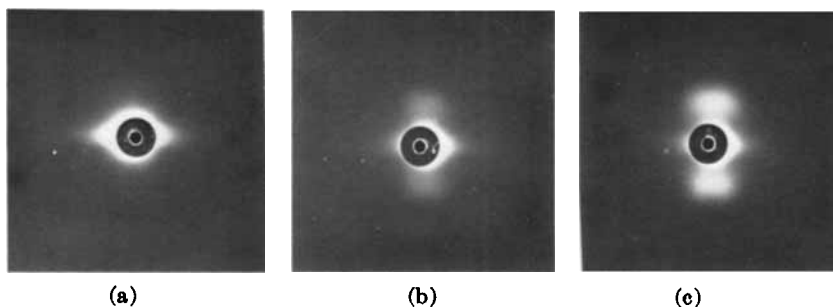


Fig. 6. X-Ray small-angle diagrams of heat-treated polyacrylonitrile fibers. Influence of annealing time (annealing temperature 240°C): (a) 10 min; (b) 60 min; (c) 300 min.

Bragg angle, radial half-width, and angular distribution of the equatorial main reflection.

The influence of annealing time on the character of the x-ray small-angle diagrams can be seen in Figure 6. The intensity of the small-angle reflections increases markedly with annealing time (annealing temperature 240°C) without any substantial influence on their shape and position.

With longer annealing times, increment in the discoloration of the fibers (from light brown to deep black) is observed.

In order to answer the question of the influence of drawing on superstructure, fibers with different draw ratios were exposed to thermo-oxidative treatment and investigated by x-ray small-angle scattering. Figure 7 shows some small-angle diagrams of fibers with a draw ratio varying from 1:3 to 1:7; the draw velocity was very fast. Obviously, the draw ratio influences shape and intensity of the small-angle reflections in a substantial manner. Intensive long-period maxima can be seen on the diagrams of fibers drawn 1:3 or 1:4, whereas these reflections are fully absent on the diagrams of fibers with a draw ratio of 1:7. It is noteworthy that a diffuse small-angle halo appears on a great number of our Kiessig diagrams. Comparative experiments were carried out with a series of fibers which had been drawn using a small hand-stretching machine (draw velocity 2–10 cm/min; draw ratio from 1:2 to 1:10). An intensive long-period reflection independent of ratio was observed on each diagram; shape and position of the reflections was influenced in a certain manner (see Fig. 8).

In order to study the influence of draw temperature on the supermolecular structure, polyacrylonitrile fibers were stretched at temperatures between 75° and 175°C with a constant draw ratio (1:4); high draw velocity). From Figure 9 it can be seen that fibers drawn at low temperatures give rise to intensive small-angle reflections. An increase in draw temperature, for example, 175°C , which is well above the technologically interesting draw temperature, prevents nearly completely the origin of a regular superstructure inside the fibers.

Small-angle diagrams of polyacrylonitrile fibers of different origin are matched in Figure 10; the results of the elemental analyses are summarized

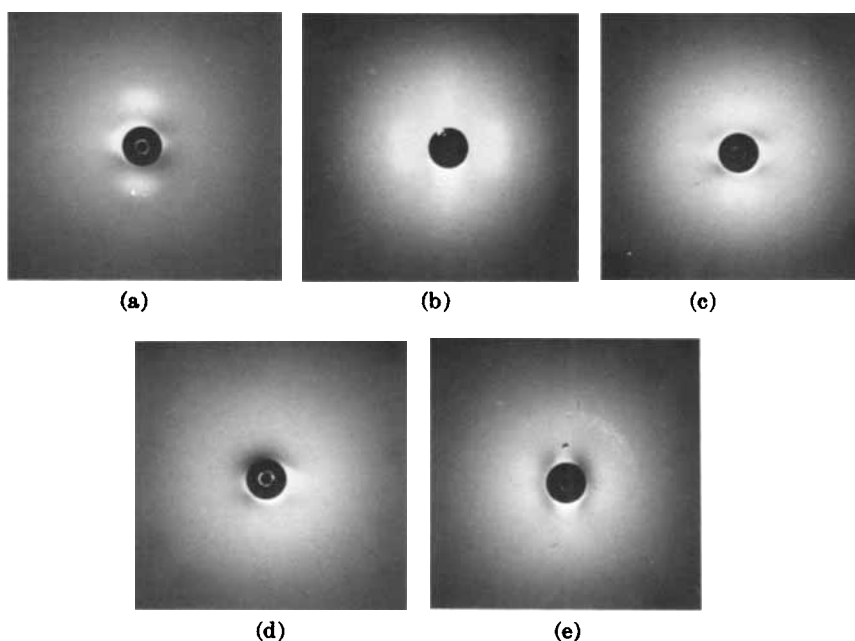


Fig. 7. X-Ray small-angle diagrams of heat-treated polyacrylonitrile fibers. Influence of draw ratio (draw temperature 100°C; high draw velocity): (a) 1:3; (b) 1:4; (c) 1:5; (d) 1:6; (e) 1:7.

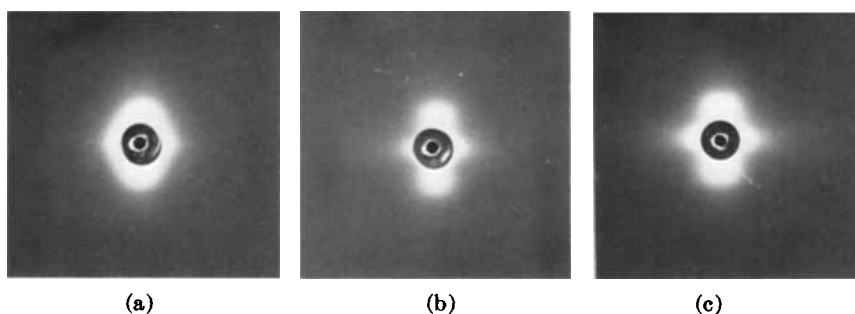


Fig. 8. X-Ray small-angle diagrams of heat-treated polyacrylonitrile fibers. Influence of draw ratio (draw temperature 100°C; slow draw velocity): (a) 1:2; (b) 1:6; (c) 1:10.

in Table II. The data of the elemental analyses (especially the oxygen content) as well as our experiences relating to the discoloration lead to the preliminary conclusion that the thermo-oxidative degradation of the specimens had been in some cases very different. Therefore, stronger differences in the intensities of the small-angle reflections as were found in the diagrams reproduced in Figure 10 can be predicted. Figure 10 shows remarkable differences of position and shape in the long-period reflections between the various fibers; the long periods calculated from the position of

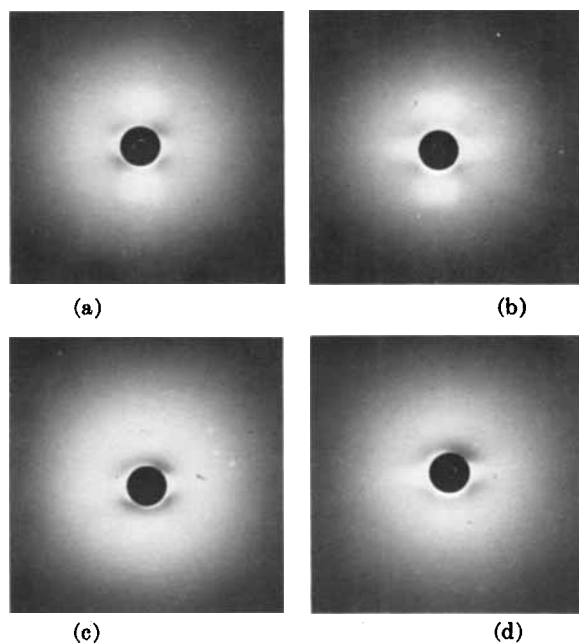


Fig. 9. X-Ray small-angle diagrams of heat-treated polyacrylonitrile fibers. Influence of draw temperature (draw ratio 1:4): (a) 75°C; (b) 100°C; (c) 150°C; (d) 175°C.

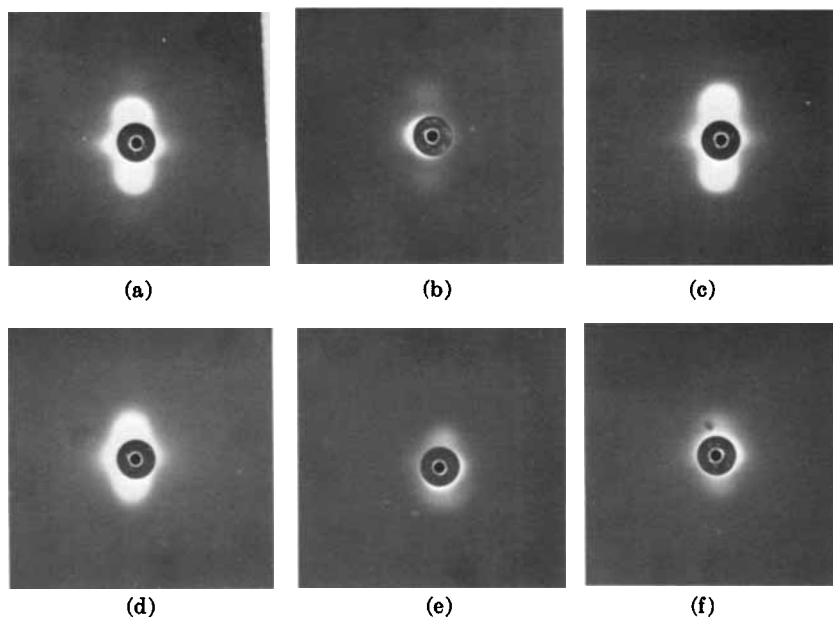


Fig. 10. X-Ray small-angle diagrams of various heat treated polyacrylonitrile fibers: (a) Orlon 42; (b) Orlon 44; (c) Dolan; (d) Leacryl; (e) Crylor; (f) Melana.

TABLE II
Results of Elemental Analysis of Polyacrylonitrile Fibers Heat Treated
in Air for 1 hour at 240°C, and X-Ray Long-Period Data

Probe	C, wt-%	H, wt-%	O, wt-%	N, wt-%	Long period, Å
Dolan	64.2	4.7	7.7	22.6	125
Orlon 42	63.8	4.7	7.0	23.6	145
Orlon 44	63.6	5.0	8.3	22.0	110
Crylor	65.0	5.3	7.1	23.0	145
Leacryl	64.1	5.2	7.6	22.8	160
Melana	66.1	5.0	4.7	23.9	145

the reflections vary from 110 to 160 Å. The shape of the reflections can be described as being nearly circular (Dolan, Orlon 42) or nearly punctate (Melana), or the scattering diagram has a four-point character (Dralon N). Without a detailed discussion of possible structure models deducible from the position, shape, and intensity of the x-ray small-angle diagrams, it shall be emphasized in summary that intensive small-angle reflections are not typical for heat-treated Dralon fibers but could be detected with all acrylic fibers treated in the described manner.

Models on the Origin of the Supermolecular Structure in Polyacrylonitrile Fibers

The results obtained in the preceding section indicate that it is possible by suitable thermo-oxidative treatment to form a superstructure inside the fibers which is manifested in the described meridional reflections. Two questions arise; firstly, why no long-period maxima can be observed with untreated fibers, and secondly, which structural changes take place during the annealing process. Before answering these two questions, it shall be briefly mentioned that according to the now valid models of x-ray scattering theory, we shall explain small-angle reflections by a periodic arrangement of regions of different electron density.

The absence of small-angle reflections with unannealed polyacrylonitrile fibers can be explained by various reasons. Firstly, it is possible—in any case, on the basis of the present experimental results—that very weak reflections exist which are lost in consequence of the photographic pickup method of the Kiessig camera. Measurements using a registering Kratky camera have to clear up this point. Secondly, it is conceivable (analogous observations on better crystallizing high polymers are reported in the literature) that with untreated drawn fibers, a weakly developed periodic structure exist. For the most investigated polymer, polyethylene, structure models are proposed by Fischer and co-workers⁶⁶ which describe the unannealed drawn material by a crystalline matrix with small amorphous regions (defects) dispersed nearly statistically; as a result of annealing near the melting point, the defects will be “exuded” and will form a second

coherent phase. Due to the disintegration of crystalline and amorphous regions, a large increase in long period intensity will be observed. Thirdly, the density difference between the more ordered (crystalline) and less ordered (amorphous) regions plays an important role with regard to the intensity of the long-period reflection because the square of the fluctuation of the electron density difference, $\langle \Delta\eta^2 \rangle$, is connected with the density difference $\Delta\rho$ by the equation

$$\langle \Delta\eta^2 \rangle = (\Delta\rho)^2 \cdot w_c \cdot (1 - w_c) \quad (1)$$

where w_c represents the degree of volume crystallinity. Therefore, for small density differences, the electron density difference and therefore the intensity of the reflection decreases. With polyacrylonitrile according to our own measurements of the crystal density in comparison to the macroscopic density, there are reliable indications that the density difference between the more and less ordered regions is small.³ Fourthly, as shown by eq. (1), the degree of crystallinity influences the electron density difference. According to eq. (1), this quantity passes through a maximum at $w_c = 0.5$. X-Ray wide-angle measurements indicate that the percentage of the more ordered phase can be estimated to be about 30%; therefore, an additional decrease in the intensity of the small-angle reflections has to be assumed. Yet our measurements on films drawn by the hand-stretching machine show that it is possible to obtain a two-phase structure with unannealed polyacrylonitrile; in this case the development of such a two-phase structure will be favored quite definitely by the extremely slow draw velocity.

In order to clear up the question of the origin of a pronounced two-phase structure as consequence of thermo-oxidative treatment, one has to discuss two possibilities:

1. The chemical changes described in detail above (cyclization, oxidation) proceed selectively, i.e., specifically either within the more ordered region or the less ordered region. The chemical reactions produce a change in electron density of that phase in which the reaction takes place preferentially, by which, according to the explanations mentioned above, an increase in intensity of the reflection is brought about.

2. Following the findings with other semicrystalline high polymers, one can suppose that with polyacrylonitrile, too, annealing close to the melting point gives rise to an intensified development of a two-phase structure and therefore to an increase in intensity of the small-angle reflection. Finally, one can imagine a combination of the two mentioned processes.

The results of our experiments hitherto in our opinion furnish insufficient evidence to decide which of the processes produces the structural change. The correlation between the appearance of a small-angle reflection and the measured increase of oxygen speaks in favor of the selective chemical degradation of one of the two phases. Furthermore, in accordance with the first suggestion, it is easier to explain that the intensity of the small-angle reflection is connected with an increase in the annealing temperature

of the specimens above 250°C because at sufficiently high temperatures the selectivity of the oxidative degradation no longer applied. Thirdly, the height of the annealing temperature which is mostly suitable for the development of a two-phase structure fits essentially better into this concept. The melting point of polyacrylonitrile is about 320°C, i.e., a temperature far from the "best" annealing temperatures (240–250°C). If the discussed decomposition causes the development of the small-angle reflection, one has to expect in contrast to the experimental results that the intensity of the reflection increases the closer the chosen annealing temperature approaches the melting point.

Finally, the important question has to be asked whether the structures observed by means of x-ray small-angle scattering after thermooxidative degradation can be correlated with those structures which exist within the unannealed samples. If the annealing gives only rise to the above-mentioned "contrasting," this question can be fully answered in the affirmative. In our opinion, the investigations on fibers which were produced with gradually changing draw ratio, draw temperature, and draw velocity produced evidence of the existence of a superstructure detectable after the annealing showing a systematic course with the manufacturing conditions. Likewise, the differences in shape, position, and intensity of the small-angle reflections from fibers of different origin point clearly to the correlation under consideration.

In publications on x-ray small-angle scattering on semicrystalline drawn polymers, experiments have been repeatedly reported where, by incorporation of molecules of high electron number (iodine, osmium, wolframate), the electron density of the amorphous phase was changed in order to bring about a stronger contrasting and, in connection with this, an increase in intensity of small-angle reflection. With reference to this technique, our thermo-oxidative treatment of polyacrylonitrile maybe designated as "auto-contrasting."

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