Optical Properties and Orientation of Thermally Treated Acrylic Fibers

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Synopsis

Acrylic fibers containing methyl acrylate copolymer have been thermally treated in the temperature range 473°–573°K in an inert, oxygen-free environment.   The optical properties and an x-ray diffraction orientation parameter have been studied in these fibers, with special attention to correlation with the essential chemical reactions and to the behavior of polymer chain orientation.   Densification of the fibers, illustrated by specific gravity and refractive index changes during the thermal treatment, is interpreted as a more efficient packing of the polymer chains in addition to the development of more highly refractive and dense chemical species.   An extrapolated value of refractive index of 1.70 for 100% nitrile polymerization supports the presence of naphthyridine structures. Birefringence changes from -0.003 to $+0.27$ imply a high degree of retention of the preferred orientation of polymer chains, despite the severe change in the chemical identity of the chains.   The contrary behavior of the orientation parameter from the 100 arc of the x-ray diffraction of polyacrylonitrile as the thermal treatment proceeds indicates that the residual polyacrylonitrile sequences have reduced orientation.

INTRODUCTION

Chemical changes taking place during the thermal treatment of polyacrylonitrile and acrylic fibers have received extensive attention.[1–18]   In the absence of oxygen, intramolecular polymerization of the nitrile groups and loss of HCN and NH_3 have been regarded as the main reactions taking place in the temperature range 470°–570°K.   Less attention has been paid to the optical properties of thermally treated acrylic fibers.[19,20]   In fibers which are stretched near their maximum elongation during or after the spinning process, the polymer chains are preferentially oriented to a high degree in a direction parallel to the fiber axis.   It has been difficult to confirm whether this preferred orientation is completely, or even substantially, retained during the thermal treatment because the chemical identity of the polymer is changing almost simultaneously with changes in physical properties.   If the fiber is not held under restraint but allowed to relax, then thermal treatment at temperatures above 450°K is known to cause a loss of preferred orientation,[21,22] which may be attributed to polymer chain relaxation and which, initially, may be independent of any observable chemical reaction.

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The present study sought to correlate physical changes taking place during inert thermal treatment of the fiber under restraint with the essential chemical reactions and to investigate, at least semiquantitatively, the effect of this thermal treatment on polymer chain orientation.

EXPERIMENTAL

Commercial acrylic fiber with a round cross section of approximately 14 μm in diameter and containing 7% methyl acrylate as copolymer was thermally treated while under longitudinal restraint by heating at 0.1°K/sec and holding at temperatures up to 573 ± 0.5°K for periods up to 1.04 × 10^5 sec. The fiber was completely immersed during this treatment in Silicone Fluid M.S. 550 (Midland Silicones Limited) which was circulated by a stream of high-purity argon containing less than 4 ppm oxygen as determined by Hersch Meter analysis. Besides providing a stringent non-oxidizing environment, the temperature control via a coil electrical heater and chrome–Alumel thermocouples immersed in the fluid was within ±0.5°K and adequately prevented thermal runaway of the fiber associated with the exothermic chemical reaction. After the treatment period, the fibers were cooled in situ and the silicone fluid removed by thorough washing with acetone under reflux. The absence of any detectable swelling and lack of even traces of silicon shown by spectrographic analysis confirmed that these liquids were inert environments for the fiber. The fiber was finally dried under longitudinal restraint for 600 sec at 413°K.

Refractive index and birefringence were determined microscopically by immersing several fibers from each sample in inert liquids of known refractive indices, viewing at magnifications up to ×1500 in plane-polarized transmitted light vibrating perpendicular and parallel to the fiber axis. The focal length technique previously applied to glass spheres [23,24] was then used. In the present case, the round filament acts as a cylindrical lens which concentrates parallel incident light above the fiber to a thin bright line or apparent focus. The refractive index is then given by the equation

$$n_f = \frac{n_m}{(1 - D)/8.4\ n_m F} \tag{1}$$

where n_f and n_m are refractive indices of fiber and immersion medium, respectively; D is the fiber diameter; and F is the apparent focal length. It is essential that the focal point should lie within the immersion medium. As the liquids in use were incompatible with the lens materials, a special mounting arrangement, illustrated in Figure 1, was used such that the depth of immersion liquid exceeded the apparent focal length of the fiber. Compensation is made for an apparent depth effect on F by inclusion of the second n_m term in eq. (1). For reasonably precise determination of F, it was necessary to choose n_m such that $n_f - n_m \leq 0.10$; n_f was then calculated to within ±0.002. Rotation of the microscope stage and specimen allowed n_f to be determined in two directions, $n_\perp$ and $n_\parallel$, when the electric
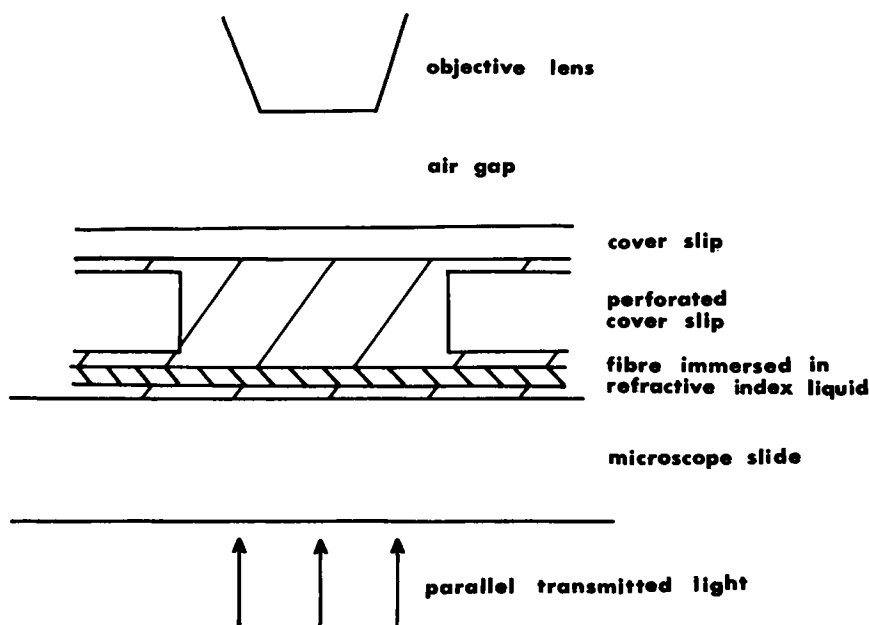
Fig. 1. Mounting arrangement for the determination of refractive indices of thermally treated acrylic fibers by the focal length technique.[23,24]

vector of the incident light vibrated normal and parallel to the fiber axis, respectively. A weighted mean refactive index is given by

$$n_{iso} = (n_\parallel + 2n_\perp)/3 \tag{2}$$

and the birefringence, by

$$\Delta n = n_\parallel - n_\perp. \tag{3}$$

The density of the fiber in chopped form was determined in duplicate by a specific gravity bottle technique using distilled water and a centrifuge treatment to remove entrained air.

A structural orientation of polyacrylonitrile in the fibers was measured by x-ray diffraction. The specimen, composed of a 0.5 mm-diameter bundle of aligned fibers under light tension, was exposed to a collimated beam of CuK_α radiation and a record of the transmission diffraction pattern made on flat photographic film placed at a distance of 50 mm from the specimen. It was essential to have the individual fibers in the bundle evenly tensioned and accurately aligned. This was achieved with a grooved specimen holder into which the fibers were cemented at the ends, using careful manipulation of the bundle to ensure wetting of each fiber with thermoplastic cement. Preferred orientation is shown by the 100 diffraction arc from the normally assumed pseudohexagonal structure of polyacrylonitrile.[25] The density variation around this arc was recorded on a Joyce-Loebl Mk IIIB micro-densitometer, from which the x-ray diffraction preferred orientation (Z°) could be determined as the angular half-width at half-peak density.

The essential chemical reaction, the disappearance of nitrile groups, was followed by infrared analysis. Chopped and powdered fiber was quantitatively incorporated into a KBr disc, and spectra were obtained on a Perkin Elmer 257 grating spectrophotometer. The 2240 cm^{-1} peak attributed to nitrile and the secondary 2190 cm^{-1} peak attributed to nitrile pendant to a conjugated chain[3,4] were used additively to estimate the relative concentration of nitrile remaining, calibrating the 2240 cm^{-1} peak with known concentrations of the untreated precursor fiber.

RESULTS AND DISCUSSION

Inert thermal treatment of the acrylic fiber generated the usual coloration from pale yellow through to deep reddish-brown with increasing duration and temperature of treatment. With thermal treatment periods up to 3.6×10^4 sec and temperatures up to 510°K, less than 2% weight loss occurred; while at longer times and temperatures from 510° to 570°K, progressive weight loss occurred up to 11.2%, accompanied by marked evolution of HCN.

Refractive index of the fiber increased from 1.512 to 1.760. Along with density increasing from 1.20 to 1.46×10^{-3} kg/m^3, this probably represents more efficient packing of polymer chains in addition to the formation of more highly refractive and dense chemical species. A correlation of the two density parameters is illustrated in Figure 2. Densification of the polymer structure is specifically related to the removal of nitrile groups, as illustrated in Figure 3. A discontinuity in the correlation reveals itself at approximately 40% of the original nitrile removed. This discontinuity is emphasized further if refractive index is plotted versus nitrile polymerized, estimated from nitrile remaining and the corresponding weight loss (assumed to be HCN evolved). Extrapolation of the linear portion to complete nitrile polymerization in both cases gives a weighted mean refractive index of 1.70, which is close to the values of 1.685 and 1.69 for naphthyridine structures, calculated from the molar refractive index data of Vogel[26] and

$$(n^2 - 1)/(n^2 + 2) = Rd/M \qquad (4)$$

where R is the molar refractive index, d is the density $(1.42 \times 10^{-3}$ kg/m$^3)$, and M is the molecular weight of the basic molecular unit (C_3H_3N and C_3HN, respectively). This suggests that structures such as
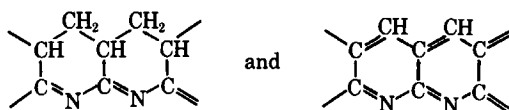
are generated by the initial chemical reaction; but this is superseded by a second reaction involving evolution of HCN and the development of structures with even higher refractive index and packing efficiency.

Birefringence of the thermally treated fibers was observed to change from −0.003 to +0.27, the highest values occurring in the thermal treatment
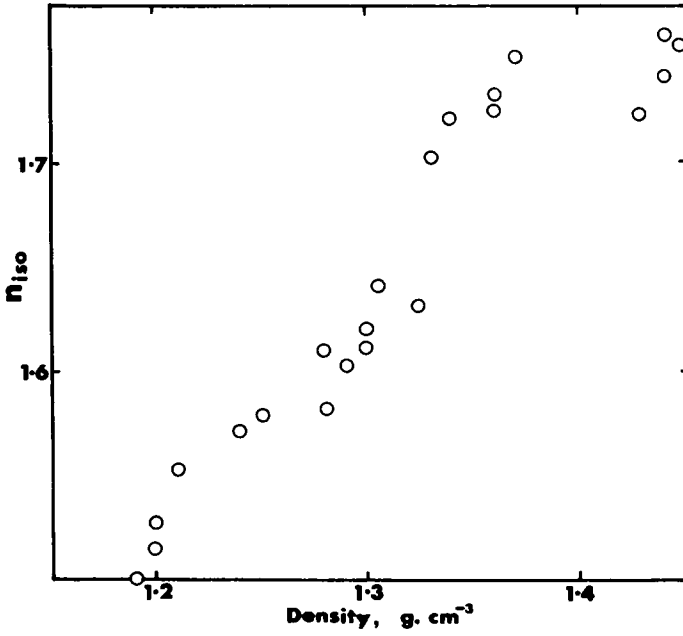
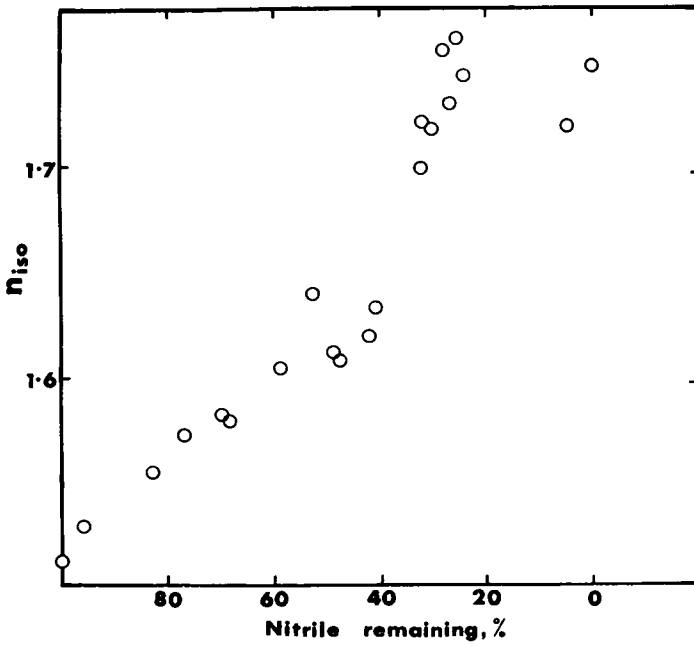Fig. 2. Refractive index (n_{iso}) vs. density of thermally treated acrylic fibers.

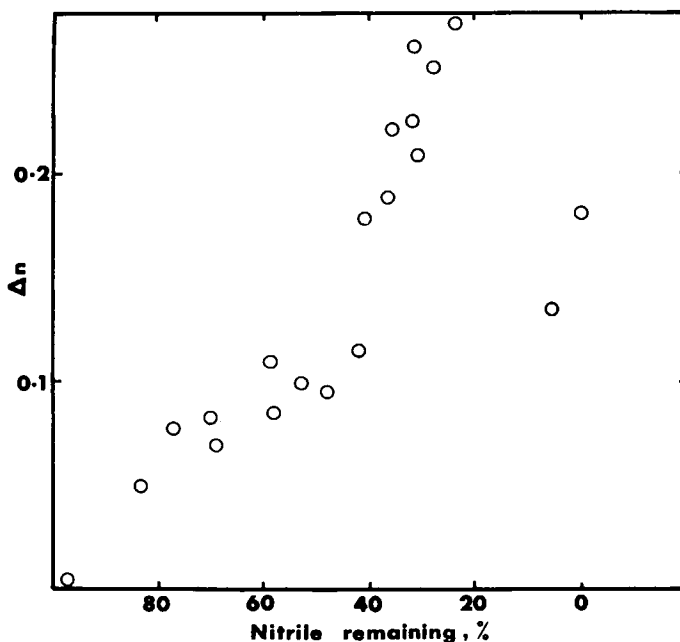Fig. 3. Refractive index (n_{iso}) vs. nitrile remaining in thermally treated acrylic fibers.

Fig. 4. Birefringence (Δn) vs. nitrile remaining in thermally treated acrylic fibers.

temperature range $500°$–$530°$K. The initial negative birefringence of acrylic fibers is attributed to pendant nitrile groups with polarizability greater than bonds in the main polymer chain[27]; but its value, usually in the range -0.001 to -0.003 in commercial acrylic fibers, must be dependant on the degree of preferred orientation of the polymer chain. A transition to positive birefringence was noted even with the removal by thermal treatment of less than 5% of the nitrile groups. The extremely high values of positive birefringence reached imply a high retention of the original preferred orientation of the polymer chains, despite the severe change in the chemical structure of the chain. A correlation of birefringence with nitrile remaining is shown in Figure 4. Similar to Figure 3, a discontinuity is apparent at 40% nitrile retained, indicative of a second reaction superseding the nitrile polymerization. It is concluded that this second reaction assists further retention of the original polymer chain orientation as well as improving polymer chain packing. On the other hand, from the samples with thermal treatment at $573°$K (less than 6% nitrile retained), it may be concluded that heating directly to temperatures above $540°$K at $0.1°$K per sec leads to some limitation in the degree of preferred orientation which can be retained, presumably because of incomplete polymerization of nitrile groups and some polymer chain scission.[17]

The qualitative evidence of birefringence in showing high retention of the degree of preferred orientation of polymer chains is supported by strong pleochroism of the thermally treated fibers, reported separately.[28]
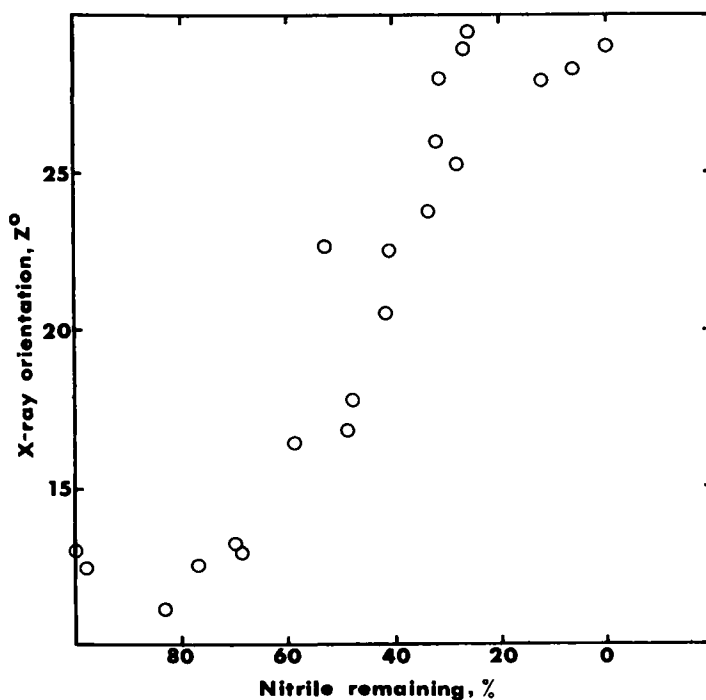
Fig. 5. Polymer preferred orientation ($Z°$) from x-ray diffraction vs. nitrile remaining in thermally treated acrylic fibers.

The x-ray diffraction patterns for the untreated fibers showed pronounced orientation of the somewhat diffuse 100 arc of the assumed pseudohexagonal polyacrylonitrile structure[25] in the preferred direction of the fiber axis. As the thermal treatment proceeded, this arc became at first fractionally sharper and more oriented and then more diffuse, extending to the region of higher diffraction angle, less intense, and less oriented; finally the arc disappeared.

The initial increase in orientation (decrease in Z from 12.9 to 11.1°), which occurred despite a loss of nitrile of up to 15% during the thermal treatment initial rise to temperatures up to 493°K, may be explained as a rearrangement of the polymer chain molecules under the influence of residual spinning and stretching stresses and made possible by the removal of the sterically most active nitrile groups. The removal of these few groups would leave the remainder appearing more ordered and oriented.

The measurements of the x-ray diffraction orientation, shown in Figure 5 as a function of nitrile remaining were recorded at the interplanar spacing (approximately 5.15×10^{-10} m) of the original precursor fiber; but, because of the features already described, values greater than 25° have limited numerical significance. The correlation of Figure 5 shows that the decreasing orientation (and the associated decreasing intensity) of the arc is specifically related to the removal of nitrile groups from the polyacryloni-
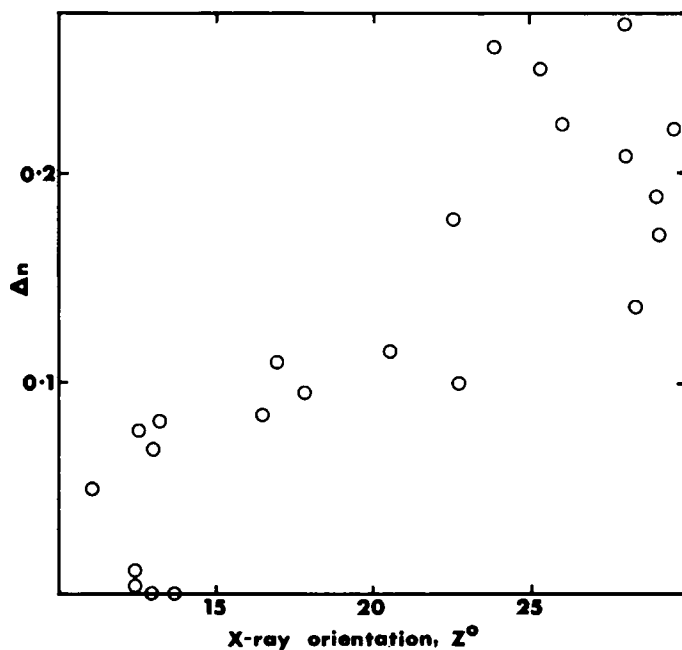
Fig. 6. Birefringence (Δn) vs. preferred orientation ($Z°$) from x-ray diffraction in thermally treated acrylic fibers.

trile structure by the polymerization and other reactions. Diffraction pattern changes are consistent with a random removal of nitrile groups from the structure which leaves the residual nitrile sequences with reduced preferred orientation. This may be due to preferred reaction of the better oriented polyacrylonitrile sequences or possibly to the polymerization reaction causing disturbance of remaining unpolymerized sequences. The dependence of the arc on the presence of nitrile tends to support the polyacrylonitrile structures of Urbanczyk[29] and Stefani.[30]

In Figure 6, a broad inverse correlation between x-ray diffraction orientation and birefringence is shown. This apparently conflicting relation is explained by the x-ray measurement reflecting the preferred orientation of the disappearing polyacrylonitrile, whereas the positive birefringence measurements reflect the preferred orientation of the new chemical species.

CONCLUSION

A study of the optical properties of acrylic fibers thermally treated under restraint in an inert environment in the temperature range 473°–573°K has shown that densification of the polymer and the development of high positive birefringence is related to the reaction of nitrile groups in polyacrylonitrile.

The correlations of refractive index and birefringence with nitrile remaining indicate that the initial nitrile polymerization is superseded by a

second reaction involving significant weight loss and evolution of HCN, which leads to further densification and, in the temperature range 500°–530°K, to the highest values of birefringence. Extrapolation of the refractive index data for complete nitrile polymerization supports the formation of naphthyridine structures with refractive indices close to 1.70. The transition from negative birefringence (-0.003) to high values of positive birefringence (up to $+0.27$) as nitrile is removed indicates a high retention of the preferred orientation of the polymer chain despite the severe change in the chemical indentity of the chain.

From x-ray diffraction data on the 100 arc of polyacrylonitrile, it appears that the residual polyacrylonitrile, in all but the initial stages of thermal treatment, has a reduced orientation. An improvement in orientation is observed only during the initial period of rise to temperatures below 500°K. The x-ray orientation parameter is specifically related to removal of nitrile, and the pattern characteristics support random reaction of nitrile groups in a pseudohexagonal structure composed of polyacrylonitrile helixes. An inverse correlation with birefringence is explained in that the x-ray parameter reflects the orientation of the residual polyacrylonitrile sequences, whereas the positive birefringence reflects the orientation of the new polymer species.

It is concluded that the preferred orientation of the polymer chains in acrylic fibers is substantially retained during the thermal treatment under the conditions of this study, at least at temperatures below about 530°K.

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