

Some Observations on the Melting Behavior of Textile Fibers. Part II. X-Ray Examination of Hot-Stretched Nylon 66

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Synopsis

X-ray diagrams of different samples of nylon passed over a hot-plate held at different temperatures show that the observed effect depends on the type of nylon used. Clear evidence consistent with the melting of the core of the nylon is obtained for monofilament.

INTRODUCTION

It has recently been shown by Farrow and Simmens¹ that nylon passed over a hot-plate, or through suitable hot liquids, can in some circumstances separate into two phases: a molten core and a highly ordered skin. The optical and mechanical measurements on nylon treated in this way have been given in Part I of this series¹; this part gives x-ray evidence for some of the hot-stretched nylon samples.

MATERIALS AND METHODS

The nylon samples used had been passed over a Scragg-type heater in the manner described by Farrow and Simmens.¹ The three samples were: 15-den. nylon hosiery monofilament heated to 199, 230, 240, 250, and 260°C.; 30/10 type-100 normal textile nylon heated to 230 and 250°C.; 840/140 type-600 high tenacity nylon heated to 230, 260, 280°C.; and also the control samples of each type.

Standard 15-mg. bundles of 1-in. long fibers were made from each sample, and preliminary x-ray photographs (Fig. 1) were taken with nickel-filtered Cu $K\alpha$ radiation in a cylindrical camera of radius 3 cm.

X-ray photographs intended for the measurement of the orientation of the samples were taken on a flat-plate camera with a film-specimen distance of 5 cm. The method employed was essentially that described by Ellis and Warwick,² except that here a camera with a collimator aperture of 0.5 mm. was used. Nickel-filtered Cu $K\alpha$ radiation was again used, but two films separated by an aluminum sheet 0.3 mm. thick were placed in the cassette. This arrangement makes it possible to take into account the effect of the white-radiation components of the x-ray beam.³

Further x-ray photographs of three samples of the nylon hosiery monofilament were taken with crystal-reflected monochromatic Cu $K\alpha$ radiation with a semicylindrical camera of radius 5.73 cm. The beam was collimated with a round collimator of aperture 0.5 mm. and after passing through the sample the beam was stopped by a piece of aluminum sheet thick enough to allow the measurement of the intensity of the main beam recorded as a spot on the film.

On all the photographs except those of the preliminary experiments a step wedge was superimposed on a blank portion of the film before processing. This subsequently provided the necessary calibration between photographic density and x-ray exposure.²

All photographs were measured with a Joyce-Loebl microdensitometer. The flat-plate photographs were measured along the equator in identical locations on the two films from the same experiment; the top film was also scanned azimuthally around the 110 and 100 equatorial reflections. The x-ray photographs taken with monochromatic radiation were measured along the equator. Wherever appropriate, the step wedges superimposed on the films were also recorded with the microdensitometer.

Since the scans along the equator of the flat-plate photographs were needed for comparison only, after being referred to the scale of x-ray exposure via the step-wedge calibration they were not further corrected. The azimuthal scans were plotted on the exposure scale, an appropriate background subtracted, and the orientation expressed as the reciprocal of the half-width of the angle at half-maximum height.

The equatorial scans from the experiments with crystal-reflected monochromatic radiation were first corrected to give the intensities in terms of x-ray exposure by means of the step-wedge calibration and then further corrected for angle, polarization, and orientation factors. It was shown by Ellis and Warwick² that the intensity J recorded at any point whose polar co-ordinates are $(\sigma_{hkl}, \beta, \omega)$ is given by

$$J = \frac{KP(\sigma\beta\omega)}{R^2\lambda^2 \sin \theta}$$

where $P(\sigma\beta\omega)$ is the density of reciprocal lattice points, K a constant, R the distance of the specimen to the point of observation, λ the wavelength, and θ the Bragg angle. For a semicylindrical camera and constant wavelength

$$J \sin \theta \propto P(\sigma\beta\omega)$$

The measured intensity J' has to be corrected for polarization by the factor⁴

$$J = \frac{J'(1 + \cos^2 2\alpha)}{1 + \cos^2 2\alpha \cos^2 2\theta}$$

where α is the Bragg angle of the plane of the monochromatizing crystal, which is here the (002) plane of pentacrythritol ($\alpha = 10^\circ 8'$).

Thus

$$\frac{J'(1.88 \sin \theta)}{1 + 0.88 \cos^2 2\theta} \propto P(\sigma_{hkl}, \beta, \omega)$$

For comparative purposes the intensity was then multiplied by the ratio of the orientation factors found for the identical samples from the other experiments so that the intensities were expressed for the same orientation as that of the blank. Finally by reference to the intensity of the spots recorded by the main beam, all the experiments could be reduced to a standard total x-ray exposure.

RESULTS AND DISCUSSION

Nylon Hosiery Monofilament

The preliminary photographs (Fig. 1) show the main effect of the heating. Comparison of the Figures 1a and 1b shows that on heating to 230°C. there is a sharpening in the x-ray pattern consistent with the assumption that the lateral order in the nylon is increased by the heating. Heating to 260°C. brings about a further stage, where, in addition to the sharper fiber pattern, there is also present an underlying powder pattern (Fig. 1c). This is consistent with the assumption that the nylon filament contains two phases, one well-ordered and oriented, the other disoriented. Other evidence previously given¹ locates these phases in the skin and core of the nylon, respectively.

The evidence from the flat-plate photographs showed that white radiation has little effect at the position of the 110 and 100 reflections. Azimuthal scans around these peaks could then be used for the measurement of orientation. However, examination of the x-ray diagram of high tenacity nylon shows that the 100 reflection is overlapped by a fairly strong reflection on the first layer-line ($\bar{1}01$) and this will therefore cause error in the azimuthal scans around the 100 reflection. It was therefore decided to use only the 110 reflection for the measurement of orientation. It is realized that all orientation factors cannot be directly deduced from this reflection, for instance the axial orientation, but nevertheless its study would indicate some of the factors operating during the heating process.

Table I gives the results for the orientation of the 110 peak of the nylon hosiery monofilament and Figure 2 shows a plot of these results. It is seen that up to 199°C. the orientation increases, then decreases to a minimum, reaches a second maximum, and again decreases. An explanation in terms of a two-phase system can be given. Initially, heating brings about better lateral order in the nylon, and along with it some improvement in orientation is found. At some point in the process the inner core of nylon starts to soften, and in this phase the orientation of the (110) plane will begin to decrease, causing the total orientation to become less than that attained at 199°C. However, when the inner phase approaches complete disorienta-

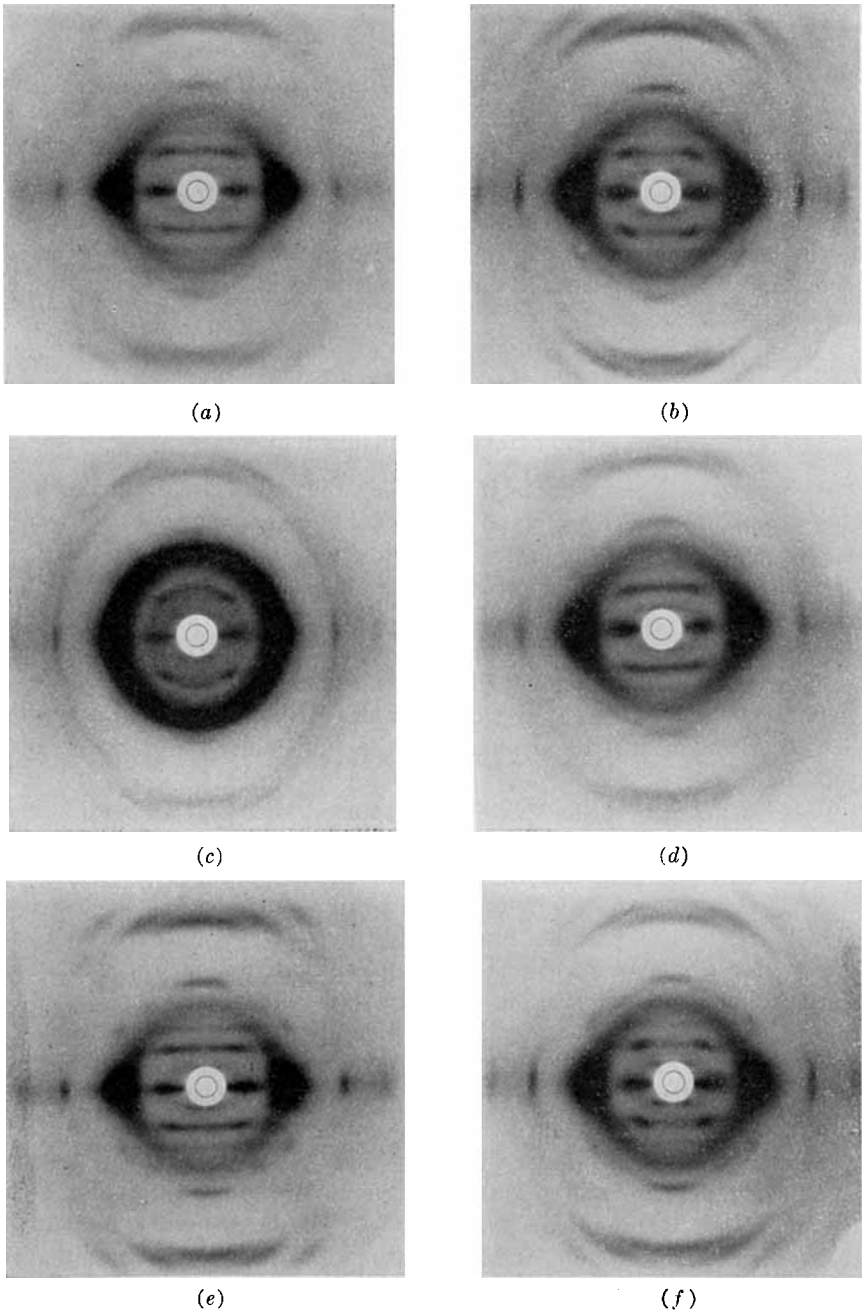


Fig. 1. X-ray photographs of nylon 66 (cylindrical camera, $R = 3$ cm., nickel-filtered $\text{CuK}\alpha$ radiation): (a) nylon monofilament (15-den.), control; (b) nylon monofilament passed over a hot-plate at 230°C.; (c) nylon monofilament passed over a hot-plate at 260°C.; (d) textile nylon (30/10), control; (e) textile nylon passed over a hot plate at 250°C.; (f) high tenacity nylon (840/140), control.

tion its contribution to the azimuthal scan will largely be to the background, so that the orientation measured will be mainly that of the oriented phase. In these circumstances the total orientation as measured here will appear to increase again until such time that the outer phase itself starts to disorient, when the orientation will drop, as is clearly shown on the graph (Fig. 2). In the range of temperatures studied, the outer phase must have retained a large measure of orientation, since at 260°C. the orientation is still high.

TABLE I
Orientation of the 110 Peak of Nylon Hosiery Monofilament

Temp., °C.	Half width ^a ϕ	$1/\phi$
Control	7.37	0.1357
199	6.33	0.1580
230	9.22	0.1085
240	8.13	0.1230
250	7.05	0.1418
260	9.61	0.1041
260	7.2 } As	0.1389 } two
	47.7 } peaks	0.021 }

^a ϕ = half-width of the angle at half-maximum height.

However, further insight into the later process can be gained by a comparison of the azimuthal scans for the control and the sample heated to 260° (Fig. 3). In all cases the orientation has been measured after the removal of the background as shown. For the control, this background is due to the general fog level of the film, air scatter, and other factors, so that the true orientation is obtained after its subtraction. For the sample heated to 260°C., besides such factors, there is the known powder ring assumed to have constant density around its circumference at any given 2θ value. A straight background incorporating the powder line and the general background can therefore be again subtracted. However, the remaining curve shape is not quite the same as originally, but can be decomposed into a peak of similar shape to that of the control and a broad peak (see Fig. 3). The orientation of the sharp peak is similar to that of the original, whereas the broad peak is clearly very disoriented (Table I). This analysis suggests that the outermost zone of the nylon after initial annealing stays constant in orientation up to 260°C., whereas an inner zone melts and there is an intermediate zone in the process of melting. These zones probably are not precisely defined but run into one another.

A knowledge of the changes in lateral order can be obtained from the equatorial scans obtained with crystal-monochromatized radiation. Figure 4 shows that the sample heated at 199°C. gives sharper peaks, increased intensity, and a shift in the peak positions as compared with those of the

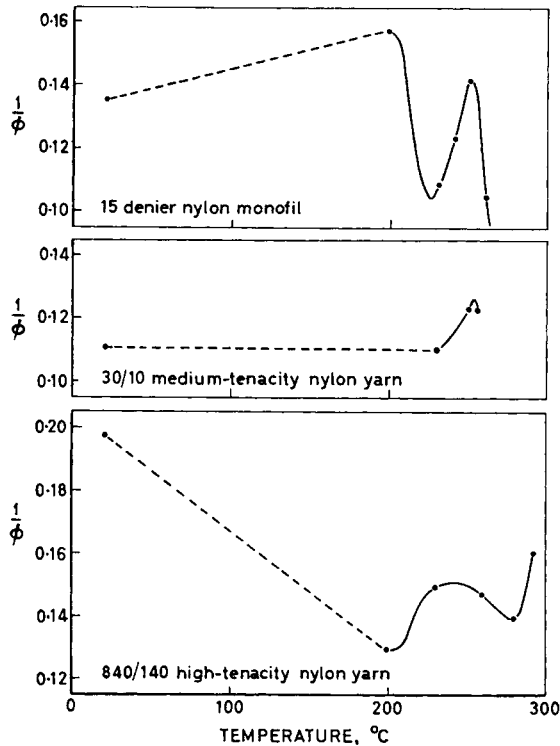


Fig. 2. The variation of the orientation of the 110 arc of nylon with temperature. ϕ is the half-width of the angle at half-maximum height on the azimuthal scan around the 110 arc; (---) denotes the region in which measurements were not made.

control. Underlying the peaks of the sample heated to 260°C. must also be a peak or peaks due to the powder line, since evidence for this is clearly given on the azimuthal scan. Nevertheless, the 100 and 110 peaks of the sample heated to 260°C. are also sharp and approximately in the same position as those found for the sample heated to 199°C.; the total intensity at the peak positions, is however less than that of the control. This latter fact is to be expected, since the inner part of the sample that originally scattered in a small arc now contributes to the scattered radiation distributed around a circle. The total diffraction at a peak position of a fiber diagram must in these circumstances be less than before.

If two broad overlapping peaks sharpen, then the expected result is that the apparent peak positions should move away from each other, and the maximum intensity of each peak should increase. This is clearly what is found here; the apparent peak positions are given in Table II. It is thus clear that even heating to 199°C. brings about better lateral order in the nylon. Whether there is also an increase in the total quantity of the three-dimensionally ordered regions cannot readily be measured, since any increase in the order in these regions themselves would reduce the

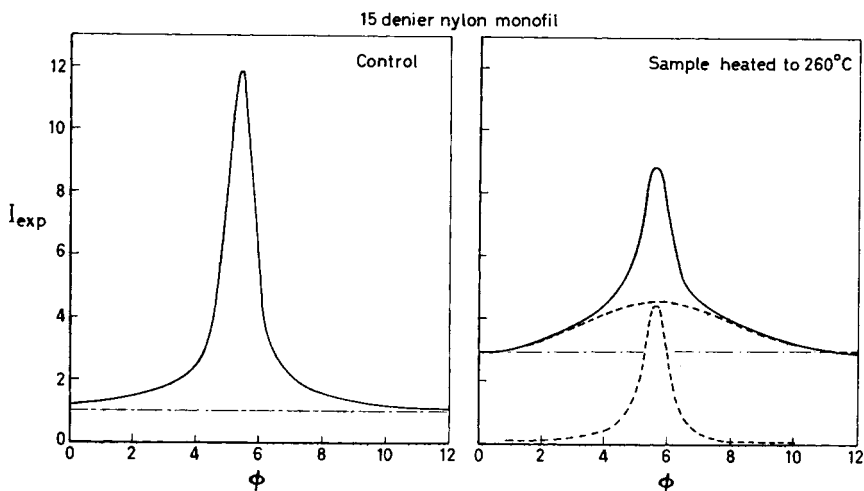


Fig. 3. Nylon monofilament (15 den.). Comparison of the azimuthal scans around the 110 arc for the control and the sample heated at 260°C.

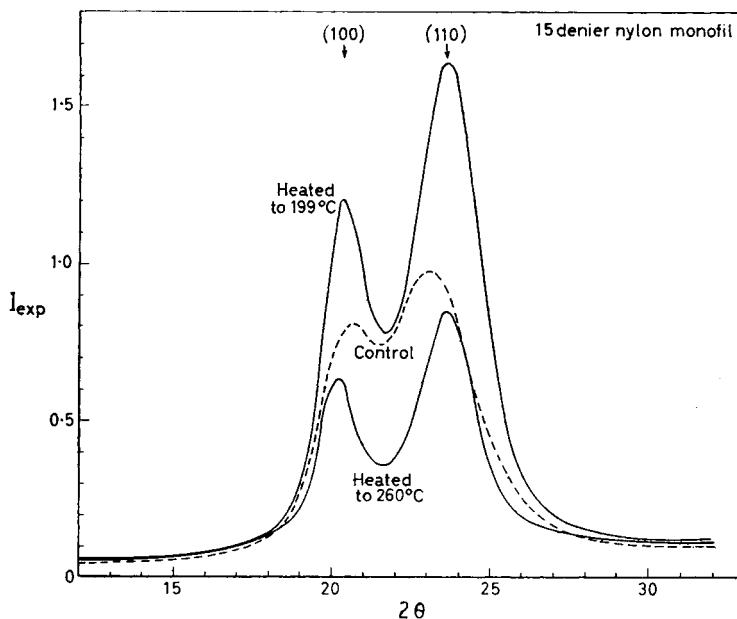


Fig. 4. Nylon monofilament (15 den.). Radial scans across the (100) and (110) equatorial arcs for the control and for samples heated at 199 and 260°C. X-Ray diagrams taken with $\text{CuK}\alpha$ radiation monochromatized by reflection from a pentaerythritol crystal.

background and increase the peak heights, without any difference being made in the total quantity of such regions. Any parameter based simply on the separation of the diffraction at the peak from that in the background

TABLE II

	2θ	
	(100)	(110)
Before heating	20.7°	23.1°
After heating to 199°C.	20.4°	23.7°

without a further analysis of the cause of the background is thus meaningless.⁵

Further heating to 260°C. reduces the peak heights, but this is due partly to the fact that portions of the material that previously only contributed to the intensity at the peak positions over a limited range of orientation now has this contribution spread around a powder ring. The fact that the peaks on the equatorial scan for the sample heated to 260°C. are still sharp shows that a reasonable portion of the material must still have high lateral order. The diffraction envelope must consist of at least three parts; the sharp peaks due to the three-dimensionally ordered and oriented material, peaks due to partially disoriented and less ordered material, and peaks from the powder lines, which themselves may be further subdivided into ordered and disordered components. A background analysis is thus complex and a true separation of the total crystalline component from the components with disorder would require further research.

It can thus be concluded that prior to zone melting the nylon improves in lateral order on heating, and even after the inner zone has melted a high degree of lateral order is still retained in a considerable portion of the material.

Multifilament Yarns

The preliminary photographs in Figures 1*d* and 1*e* for normal textile nylon (30/10) show that some improvement in lateral order is brought about by heating. The effect of heat on high tenacity nylon is less noticeable in the preliminary photographs, and therefore only one x-ray diagram of this type of nylon has been included (Fig. 1*f*).

X-ray diagrams with the flat-plate camera are less informative about the effects of heat with nylon from multifilament yarns than with monofilament. This is to be expected, since under the conditions of heating in these experiments some filaments in the yarn receive more severe heat treatment than others in the same part of the yarn, and, since x-ray results are mean results, the effect of heat on individual filaments is obscured.

The equatorial scans show a separation and sharpening of the main peaks when normal textile nylon (30/10) is heated to 230°C. It must be emphasized that the temperatures quoted are those of the hot-plate, so that temperatures in the yarn will vary with location. For the control sample the main equatorial peaks appear at 2θ values of: 21° (100) and 23.2° (110), but for the sample heated to 230°C. these values are 20.9° and 23.6°,

respectively. No appreciable change is found for yarn heated to 250°C., for which $2\theta = 20.6(100)$, $23.8(110)$, and to 255°C., for which $2\theta = 20.4(100)$, $23.8(110)$, but the peaks appear to be sharper and better separated.

The orientation of the 110 peak is the same for the sample heated to 230°C. as for the control, but whether any changes can take place at intermediate temperatures is not known. At 250°C. there is an increase of orientation (Table III and Fig. 2), and at 255°C., just before the yarn breaks, the orientation is not significantly different from that at 250°C. However, there is now evidence of powder rings underlying the main peaks as was found with monofilaments when core melting had taken place. It is therefore probable that the orientation is at its maximum between 250 and 255°C. and thereafter would be found to be lower as melting is approached. Unfortunately it is difficult to obtain specimens without breakage after 255°C., and hence 255°C. is the highest temperature that can conveniently be used with this yarn.

TABLE III
Orientation of the 110 Peak of Normal Textile Nylon (30/10)

Temp., °C.	Half-width ^a ϕ	$1/\phi$
Control	9.04	0.1106
230	9.07	0.1103
250	8.10	0.1235
255	8.13	0.1230

^a ϕ = half-width of the angle at half-maximum height.

The x-ray results alone cannot prove that core melting has taken place because other explanations are possible. Thus, with a multifilament yarn, the component filaments receive different heat treatments according to their position in relation to the heat source. It is therefore possible to obtain a yarn with some filaments completely disoriented just before melting close to filaments that have been annealed, and this state of affairs would give a very similar x-ray analysis to a monofilament with core melting present. Furthermore, other distributions of core-melted filaments, annealed filaments, disoriented filaments, and unchanged filaments could be present. However, optical examination of the yarn by Farrow and Simmens¹ confirmed that core melting had actually taken place in some filaments in the yarn heated to 255°C. That other possibilities outlined above can exist, however, must not be ruled out.

A further factor arises when high tenacity nylon (840/140) is used. The first effect is a drop in orientation (Table IV and Fig. 2) towards that found for normal nylon and this is probably due to the relaxation of internal strains promoted by the high temperature. It is unlikely that this process varies continuously with temperature, and it probably sets in at a critical temperature, which is unknown. The graph of orientation between 20 and 200°C. is thus only intended to show that the fall in orientation takes place

TABLE IV
Orientation of the 110 Peak of High Tenacity Nylon (840/140)

Temp., °C.	Half-width ^a	
	ϕ	$1/\phi$
Control	5.06	0.1976
200	7.73	0.1294
230	6.71	0.1490
260	6.8	0.1471
280	7.16	0.1397
286	6.22	0.1608

^a ϕ = half-width of the angle at half-maximum height.

in this region. During and after the process of relaxation there will be an additional process of annealing, with this taking prominence at higher temperatures so that the orientation of the (110) plane will start to increase again to a maximum. However, as the temperature is raised some filaments in the yarn will begin to melt, and this will eventually cause a drop in the mean orientation of the yarn, until melting of these filaments is complete at still higher temperatures, leaving mainly annealed filament and thus having the effect of again increasing the mean orientation. There must be a drop in the mean orientation ultimately to zero when the whole yarn begins to melt, but this stage has not been reached here.

Optical examination of the yarn at the different stages confirms that at the higher temperature some of the filaments that are close to the hot-plate melt, whereas others remain apparently unaffected. The effects noted can therefore be readily explained without reference to the phenomenon of core melting. However, if individual filaments are heated under special conditions it has been found by Farrow and Simmens¹ that core melting can be detected.

It can thus be concluded that the effect of heat on nylon depends on the type of nylon and also on the way in which the heat is applied. Core melting is therefore more likely to occur with monofilament nylon than with multifilament nylon, for reasons that are discussed in Part I.¹

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Résumé

Les diagrammes de rayons-X de différents échantillons de nylon, que l'on a fait passer sur une plaque chauffante portée à différentes températures, montrent que l'effet observé dépend du type de nylon utilisé. Pour du monofil on montre clairement que c'est la fusion du centre du nylon qui se produit.

Zusammenfassung

Röntgendiagramme von verschiedenen über eine heisse, verschieden temperierte Platte geführten Nylonproben zeigen, dass der beobachtete Effekt vom verwendeten Nylontyp abhängt. Bei Monofilamenten wird der eindeutige Nachweis für das Schmelzen Nylonkerns erbracht.

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