

Structure Development during the Heat-Draw Process of Nylon 66 Fiber by Synchrotron X-ray Diffraction

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ABSTRACT

On-line studies of structural development during continuous drawing of nylon 66 fiber at different temperatures were carried out using synchrotron wide-angle X-ray diffraction (WAXD). A unique image analysis method was introduced to analyze the two-dimensional (2D) WAXD patterns. The quantitative fractions of crystal, mesomorphic and amorphous phases were obtained. In this study, the Brill transition during nylon 66 fiber deformation was observed. From our analysis, we confirmed the existence of a premelting process in the vicinity of the Brill temperature. However, this premelting process may not have any correlation with the Brill transition. Results also indicate that drawing can stabilize the crystal and mesomorphic phases.

INTRODUCTION

Nylon 66 has been known to undergo a Brill transition, where the two strongest equatorial reflection peaks in an X-ray diffraction pattern merge into a single peak at the Brill transition temperature (T_B)¹. Bunn and Garner² have shown that at room temperature, the structure of nylon 66 is triclinic ($a = 4.9 \text{ \AA}$, $b = 5.4 \text{ \AA}$, $c = 17.2 \text{ \AA}$, $\alpha = 48.5^\circ$, $\beta = 77^\circ$, $\gamma = 63.5^\circ$). At high temperatures (above 453 K), this structure is still triclinic, but the cross-sectioned projection normal to the c-axis has a hexagonal symmetry^{1,3}. Early studies reported that at high temperatures, two-dimensional hydrogen-bonded sheets were converted into a three-dimensional hydrogen-bonded network with hexagonal packing^{1,3-4}. Other studies indicated that this might not be the case, as the hydrogen-bonded amides are relatively immobile at high temperatures (above T_B , but less than 503 K)⁵⁻⁷. In addition, some studies proposed that the Brill transition was accompanied by a first-order thermodynamic transition⁸⁻¹⁰. Recently, Hsiao *et al.*¹⁰ suggested that a premelting process of small (or defective) crystals preceded the Brill transition during fiber deformation at high temperatures.

Many recent findings¹¹⁻¹³ suggest that the fiber structure should include an intermediate phase between crystalline and amorphous fractions, which may be due to the lattice dislocations of one- or two-dimensional ordering in the crystal phase or the oriented amorphous chains. The

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intermediate phase (termed mesophase) represents a state of order between the zero long range ordering (amorphous state) and the three-dimensional (3D) crystalline ordering. However, up to now, there has been no effective method to separate this mesophase from the crystalline component. In this work, a novel image analysis of the 2D WAXD pattern has been used to determine the fractions of crystal, mesomorphic, and amorphous phases. Several new insights into the effect of drawing on structure development in nylon 66 fibers have been obtained from this study.

EXPERIMENTAL

Synchrotron wide-angle X-ray diffraction (WAXD) measurements were carried out at the X3A2 SUNY beamline, National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (BNL). The wavelength used was 1.54 Å. A 3-pinhole collimator system¹⁷ was used to reduce the beam size to 0.6 mm in diameter. The 2D detector for WAXD measurements was a MAR CCD x-ray detector (MARUSA). The distance between sample and detector was 116.8 – mm, which was calibrated by using a Lupolen standard. The collection time for each image was 2 min. The chosen nylon 66 fiber (1J270) was an experimental sample provided by DuPont.

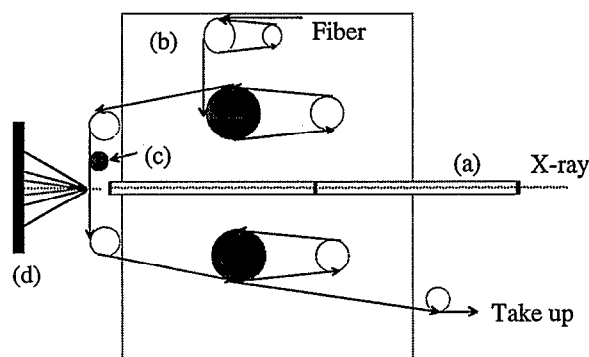


Fig.1 Schematic diagram of the continuous draw apparatus for the on-line WAXD measurement. (a) three-pinhole collimator (b) draw apparatus with continuous feed yarn (c) hot-pin (d) MARCCD detector.

A compact continuous fiber draw apparatus was built for on-line synchrotron X-ray studies of different fibers (Fig.1). It was originally designed by Dr. A. D. Kennedy of DuPont and constructed by Hills Inc., Melbourne, Florida. The drawing speed was maintained at 4 meters/min, while the feeding speed was continuously adjusted to achieve the desired draw ratio. Draw ratios ranged from 1.00 to 1.25. Two temperature-controlled heat pins were located along the fiber drawing path.

DATA ANALYSIS

For the drawn fiber, the 2D WAXD pattern (after correction for the background and the air scattering) can be deconvoluted into two fractions: isotropic and anisotropic parts. The isotropic part includes the amorphous phase and the Compton scattering from the chemical structure, which is small and may be ignored. The isotropic fraction $A_{iso}(s)$ can be obtained using the "halo" method: starting from the center of the diffraction origin, an azimuthal scan is drawn

along the angular axes (2θ). At each angular pixel position, a minimum diffraction intensity value is obtained from an azimuthal scan, eventually yielding an intensity envelope for the isotropic fractions as one moves along the angular axis. The anisotropic contribution in WAXD consists of a crystal phase and a mesophase. The deconvolution of the anisotropic fraction $A_{an}(s, \phi)$ is based on the following equation:

$$A = A_{iso}(s) + A_{an}(s, \phi) \quad (1)$$

where A is the total scattering and $s = 2\sin\theta/\lambda$ is the scattering vector, with 2θ being the scattering angle.

The anisotropic fraction can be further deconvoluted into mesomorphic and crystal fractions by using the method of two-dimensional peak fitting. Assuming that both the crystal phase and the mesophase can be described by a two-dimensional Gossip function, the generalized expression for each 2D function becomes

$$f = h \cdot \exp\left(-\left(\frac{x_0 - x}{\omega_x}\right)^2 - \left(\frac{y_0 - y}{\omega_y}\right)^2\right) \quad (2)$$

where the subscript "0" represents the peak position, ω is the full width at half maximum, h represents the height of the peak. In a polar coordinate system (r, ϕ), there are following relations: $x = r\sin\phi$ and $y = r\cos\phi$. The widths along the r axis and ϕ axis are related to the size and orientation information of each reflection, respectively.

A unique software package has been developed by us to extract quantitative information on the fractions of crystalline, amorphous and mesomorphic phases from the two-dimensional diffraction pattern by using this image analysis method.

RESULTS AND DISCUSSION

Typical 2D WAXD patterns during fiber drawing at different temperatures are shown in Fig.2. Fig.2A shows two strong reflection peaks, (110) and (010)-(110) doublet, in the equator at 373 K. The corresponding one-dimensional plot is shown in Fig.3 which can be fitted by two crystal peaks (peak 2 and 3) and one amorphous peak (peak 1). However, above 425 K, changes occur in WAXD. Two strong equatorial reflection peaks in the fiber pattern are found to converge into a single peak, which is known as the Brill transition. This change is step-like and not continuous, indicating that the Brill transition is related to a first-order behavior. This is consistent with the studies by Ramesh & Keller et al.⁹ and Hsiao et al.¹⁰.

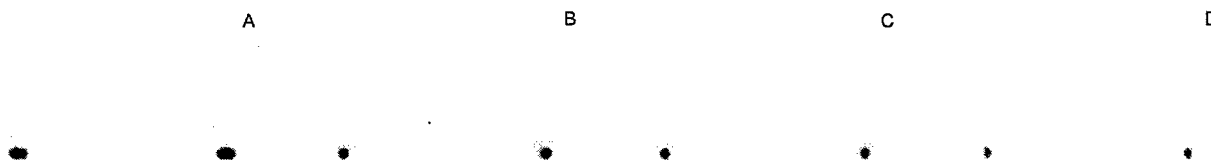


Fig.2 Nylon 66 fiber 2D WAXD images collected at draw ratio = 1.13 and different draw temperatures: A: 373 K B: 425 K C: 453 K D: 486 K.

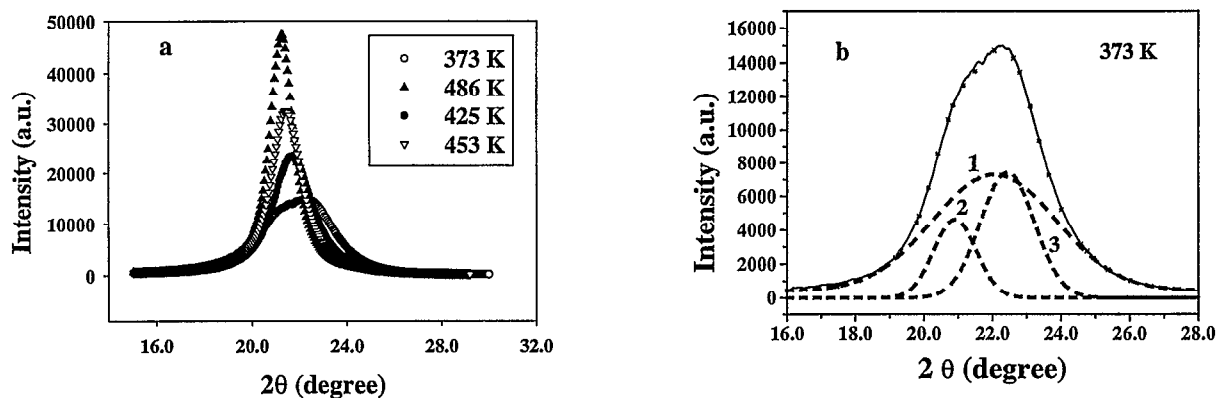


Fig.3 The corresponding one-dimensional plots (a) of the 2D patterns at different temperatures. (b) is the peak fitting of the pattern at 373 K. The solid line is the experimental data, the dash line represents the fitting plot.

Fig.4 shows fractions of crystal, amorphous, and mesomorphic phases at different draw temperatures. With increasing temperature, the crystal fraction is seen to first decrease, then increase, and finally decrease. The amorphous fraction shows an opposite trend. This suggests that some small crystals melt under tension at lower temperatures first. These small crystals probably originate as a result of secondary crystallization according to the work by Hisao et al.¹⁰, which is common in most unoriented semi-stiff polymers such as nylon 66¹⁵. Hsiao et al.¹⁰ pointed out that there was a premelting process before the Brill transition based on the behavior of the unit cell parameters. In this study, the decreasing crystal and increasing amorphous behaviors have also confirmed the existence of the premelting process. In Fig.2, the Brill transition appears to occur between 373 K and 425 K. (Herein we caution that all the temperatures referred to are the set temperatures at the draw machine hot-pin. The fiber temperature at the X-ray detection position is lower than the set temperature due to the heat loss.) The notion that the premelting process preceded the Brill transition¹⁰, however, may be incorrect according to our results. It is seen that the premelting process persists (> 425 K) even after the Brill transition (373 K~ 425 K). With these observations, we have reached the following conclusions. As the Brill transition is a structural change inside the unit cell and the premelting process occurs in the whole lamella, these two phenomena may not be correlated. Beyond the Brill transition temperature, the crystal fraction is found to increase and the amorphous phase to decrease, indicating that there is recrystallization. At the higher temperature, the recrystallization becomes more difficult because the mobility of the chains increases. Meanwhile some larger crystals begin to melt, which results in a slight decrease in the crystal fraction. The increase of the amorphous phase at higher temperatures is mainly due to the decrease of the mesophase.

The mesophase is disordered when compared with the crystal structure¹⁶⁻¹⁷, but still may have one or two-dimensional order(s). When the fiber is drawn, the longer chains will probably form either extended chain crystals or mesophase with molecular orientation aligned with the fiber axis. The shorter chains will form fold chain crystals at a later stage probably through an epitaxial growth between the extended chain crystals¹⁸. With increasing temperature, the mesophase shows the same trace as the crystal phase: first decrease, then increase and decrease

again. This indicates that the mesophase is not a stable phase (it is metastable). From our results, we conclude that the mesophase can transform into the amorphous phase, but not into the crystal phase.

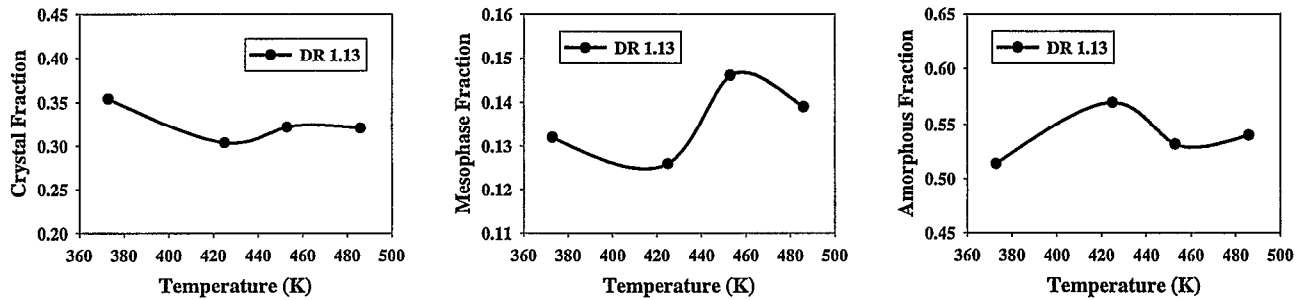


Fig.4 Fractions of crystalline, mesomorphic and amorphous phase as functions of temperature at draw ratio 1.13.

Fig.5 shows the effects of the draw ratio on the fractions of crystal, mesomorphic and amorphous phases. The fractions of crystal and mesophase are found to increase and the amorphous phase to decrease with increasing draw ratio. At different temperatures, the results show the same trend. An increase in the draw ratio prevents the melting of the crystals. These findings indicate that the tension can stabilize the crystal and mesophase, retarding the transitions between the crystal or the mesophase with the amorphous phase.

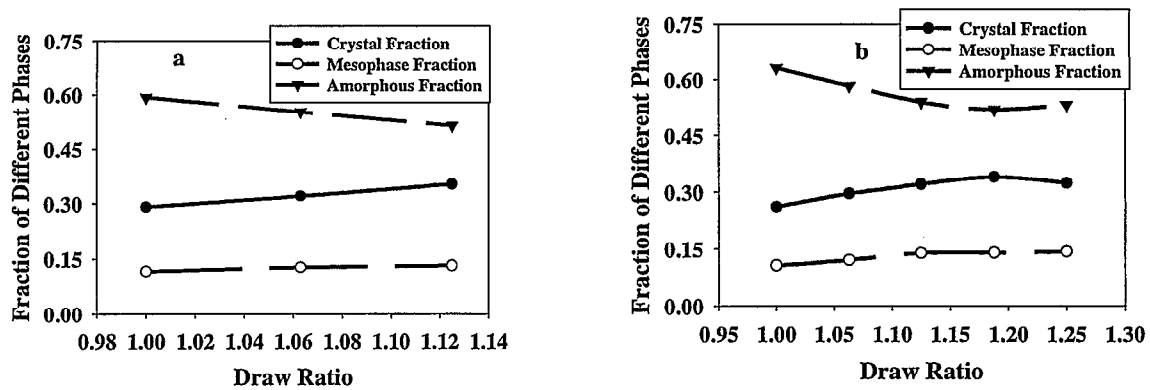


Fig.5 Fractions of crystalline, mesomorphic, and amorphous phase at different draw ratios. (a) T = 373 K; (b) T = 486 K.

CONCLUSIONS

In this work, the Brill transition during nylon 66 fiber deformation was observed. The quantitative fractions of the crystal, mesomorphic and amorphous phases were obtained by using the unique image analysis method. From our analysis, we confirmed the existence of a premelting process. However, this premelting process may not have any correlation with the

Brill transition. Drawing was found to stabilize the crystal and mesomorphic fractions in the fiber.

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