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Changing of the Crystal Structure of Nylon 6 Drawn under High Pressure

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ABSTRACT

Nylon 6 filaments were drawn under high pressure. By means of wide-angle x-ray diffraction and differential scanning calorimetry, nylon 6 fibers were investigated after drawing at 80°C to a draw ratio of 3.75 and pressure in the range of atmospheric up to 2000 kg/cm^2. It was found that by increasing the pressure, structural conversion from the γ-pseudohexagonal to the α-monoclinic form occurs, and that crystallinity and orientation are also increased.

INTRODUCTION

Nylon 6 fibers are one of the most important commercially produced man-made fibers. Fabrication conditions determine the microstructure and physical properties. The potential usefulness of nylon 6 fibers can be optimized by appropriate control at extrusion, orienting, and annealing. Nylon 6 can exist in either of two stable crystal structures, the α-crystal with hydrogen bonds between antiparallel chains

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and the γ-crystal with hydrogen bonds between parallel chains. Nylon 6 can also exist in a series of metastable crystal structures which vary continuously in size, perfection, and structural parameters from a pseudohexagonal structure to either of the two stable forms. Nylon 6 should not be considered as a pure structure because below its melting point one may distinguish not only well-formed α- and γ-crystalline forms, but amorphous polymer and disordered α- and γ-forms [2]. Although nylon 6 has been known for 40 years, considerable confusion still remains in the literature concerning the nature and stability of the various crystalline forms that this important material may assume. This aspect of the problem has recently been reviewed by Parker and Lindenmeyer [3]. A reasonable rationaliztion is that there exist only two basic crystallographic forms, α and γ, in nylon 6. The pseudohexagonal γ form is produced when the melt is rapidly quenched, and this may be converted into the monoclinic α-form by annealing or drawing. An oriented γ-form can be produced directly from melt spinning at high speeds. The γ-forms cannot be reconverted to the α-form by a conventional annealing step [4-10].

In order to learn more about crystal structure of nylon 6 filaments, we have studied crystal transformation, orientation, and crystallinity during drawing under high pressure in the range up to 2000 kg/cm^2. The techniques used to characterize the structure included x-ray diffraction, wide-angle x-ray scattering (WAXS), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Sample

A commercial undrawn nylon 6 fiber (Teijin Co. 9000d) was used in the present work. High-pressure drawn samples of nylon 6 fiber for x-ray and DSC studies were prepared by using the apparatus shown in Ref. 1. Silicone oil was used as the pressure-transmitting fluid. High-pressure drawing was performed at 80°C and a drawing ratio of 3.75 under applied pressures of 500, 1000, 1500, and 2000 kg/cm^2. Before drawing, nylon 6 as spun fiber was heated in silicone oil for 20 min. After drawing, the samples were removed from the apparatus, washed with acetone to remove silicone, dried, and conditioned for 72 h at 20°C and 65% relative humidity. Other samples were drawn at 80°C, a 3.75 draw ratio, and atmospheric pressure. They were subjected after drawing to the same procedure mentioned before. All samples were annealed at 180°C for 2.5 h in a vacuum oven. Then x-ray and DSC measurements were performed.

X-Ray Measurements

Wide-angle x-ray diffractograms were obtained with a Rigaku Denki model x-ray diffractometer equipped with a scintillation counter. The x-ray source was nickel-filtered CuKα radiation (35 kV, 30 mA). The equatorial scans in the range 2θ = 5-30° were made with the fiber axis perpendicular to the x-ray beam. In all cases the diffractometer scan rate was 1°/min.

WAXS photographs were taken on a Rigaku Denki small-angle camera equipped with a wide-angle cassette. The sample-film distance was 30 min. The x-ray source was nickel-filtered CuKα radiation (40 kV, 120 mA).

Differential Scanning Calorimetry

For DSC measurements, a 5-mg sample of the drawn nylon 6 fibers under high pressure was analyzed with a Rigaku TG-DSC model at a heating rate of 10° C/min and at a sensitivity of 4 mcal/s per full-scale deflection. For the calculation of heat of fusion (ΔH), the following equations were used:

$$\Delta H = \frac{KA}{M}; \qquad A = A' \frac{12a}{25b}$$

where M = weight of the sample in mg, A' = area of the peak in mm^2, a = DSC range (±) in mcal/s, b = chart speed in mm/min, and K = apparatus constant.

RESULTS AND DISCUSSION

Nylon 6 filaments melt spun through ordinary air or air saturated with moisture crystallize on the bobbin, not in the spinline, and the rate of this process depends on the molecular orientation developed by the spinning conditions. After conditioning in a humid atmosphere, all of the spun filaments partially crystallized into the γ-form. This is attributed to the plasticizing action of water molecules which increase the chain mobility. Figure 1 shows the WAXS pattern of our undrawn sample. It shows a pattern with two readily observable but broadened reflections at d spacings of 8.2 and 4.13 Å. The 8.2 Å spacing is meridional, and the 4.13 Å spacing is most intense at the equator though a complete faint ring may be observed. Its diffractometer scan shows a broad single peak (Sample a). The notation b and c in Fig. 1 show WAXS patterns and diffraction scans of the drawn and annealed samples under atmospheric pressure. The

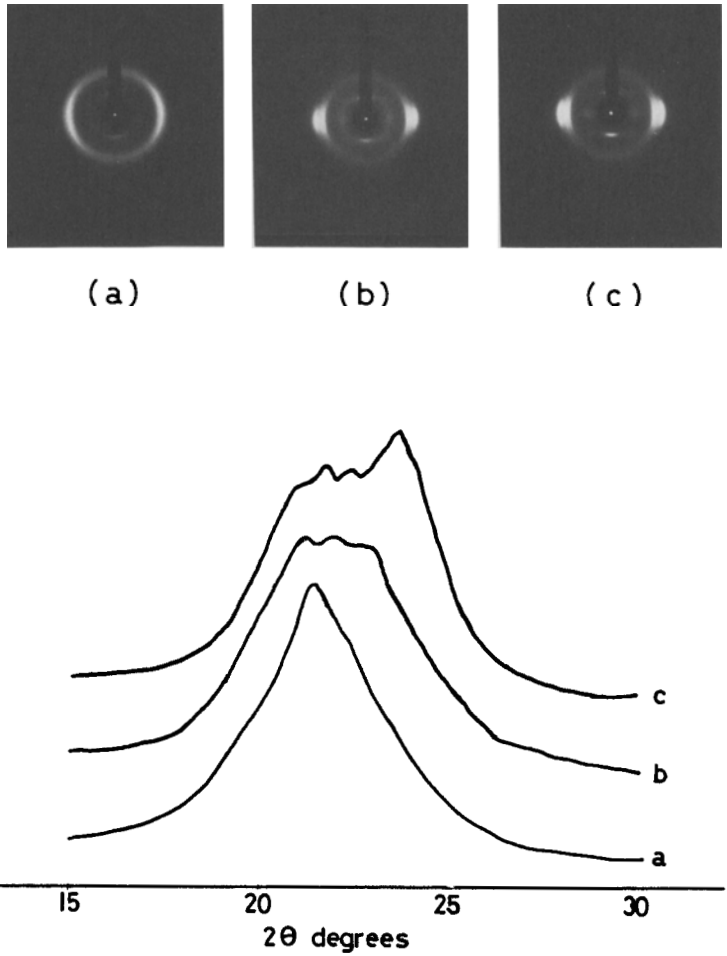

FIG. 1. Equational diffractometer scans for nylon 6 filaments. The curves have been shifted along the vertical coordinate for clarity: (a) undrawn sample, (b) drawn sample at atmospheric pressure, and (c) Sample b annealed 2.5 h at 180°C. WAXS patterns for a, b, and c samples.

pattern has readily observable 200 and 002, 202 equatorial reflections of the α-structure and 100 equatorial and 002 meridional reflection of the γ-structure.

Figures 2-5 show WAXS patterns and equatorial diffraction scans of drawn samples under high pressure in the range of 500, 1000, 1500, and 2000 kg/cm^2, respectively. The WAXS patterns indicate a

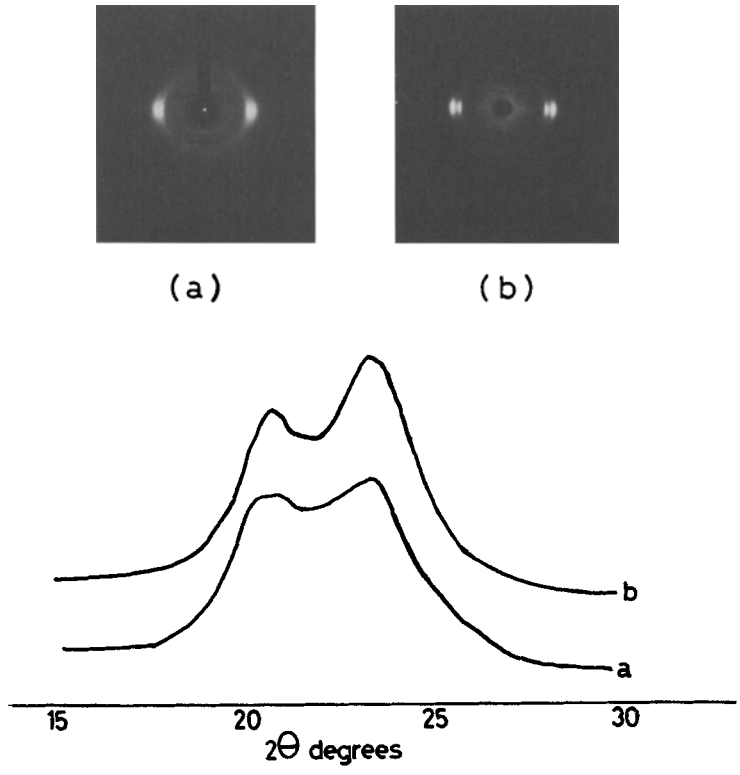

FIG. 2. Equatorial diffractometer scans. (a) Drawn sample under 500 kg/cm^2 pressure, and (b) Sample a annealed 2.5 h at 180°C. WAXS patterns for a and b samples.

transformation from the pseudohexagonal γ-form to an α-monoclinic structure. The equatorial 100 reflection of the pseudohexagonal structure appears to split into two peaks which can be indexed as 200 and the doublet 002, 202 of the α-form. The peaks on the diffraction scans become more clearly distinguished with increasing pressure. It is shown in Fig. 5 that the diffraction scan has two peaks, from left to right, associated with the 200 planes of the α-form at $2\theta = 20.3°$ and the 002, 202 planes of the α-form at 23.8°. Heat of fusion is plotted against applied pressure in Fig. 6. This shows a change of the heat of fusion measured by DSC with a change of drawing pressure. It is seen that an increase in crystallinity occurs due to the pressure treatment. These trends correspond to sharper diffraction scans with increasing pressure. We have measured the 0,14,0 reflection, which has a measurable intensity only in an oriented fiber [2]. For

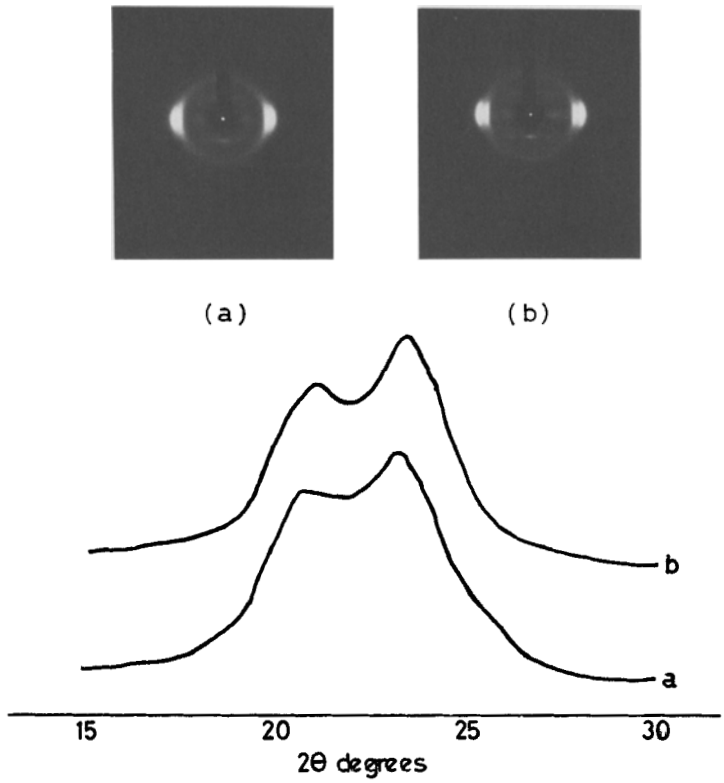

FIG. 3. Equatorial diffractometer scans. (a) Drawn sample under 1000 kg/cm^2 pressure, and (b) Sample a annealed 2.5 h at 180°C. WAXS patterns for a and b samples.

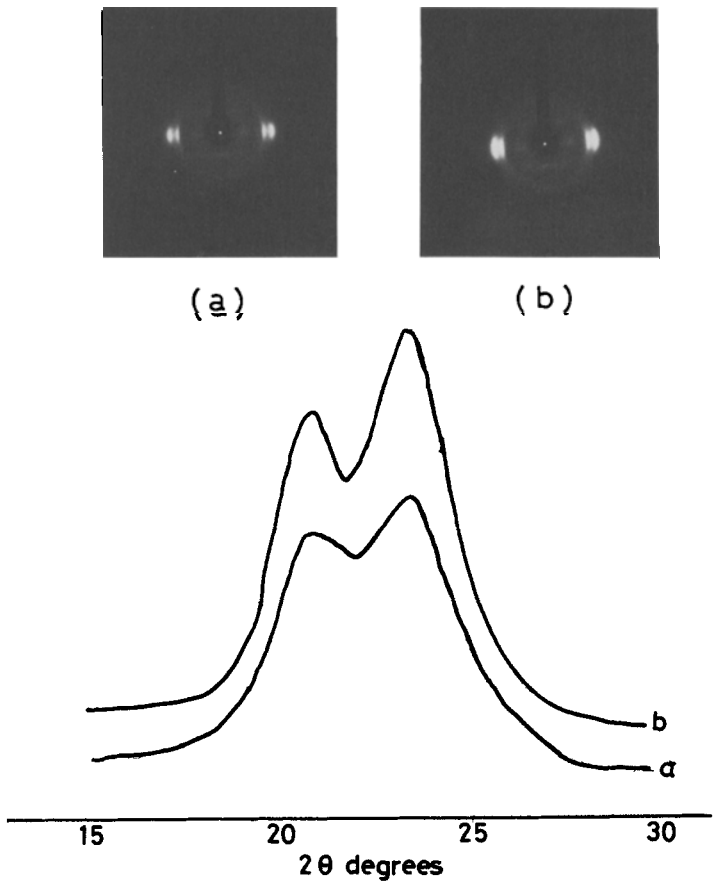

FIG. 4. Equatorial diffractometer scans. (a) Drawn sample under 1500 kg/cm^2 pressure, and (b) Sample a annealed 2.5 h at 180°C. WAXS patterns for a and b samples.

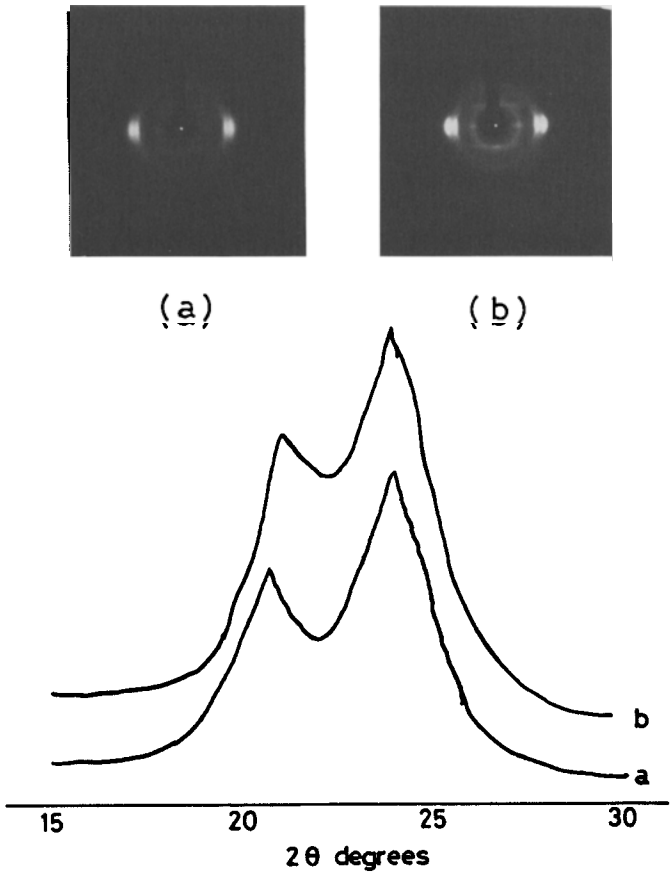

FIG. 5. Equatorial diffractometer scans. (a) Drawn sample under 2000 kg/cm^2 pressure, and (b) Sample a annealed 2.5 h at 180°C. WAXS patterns for a and b samples.

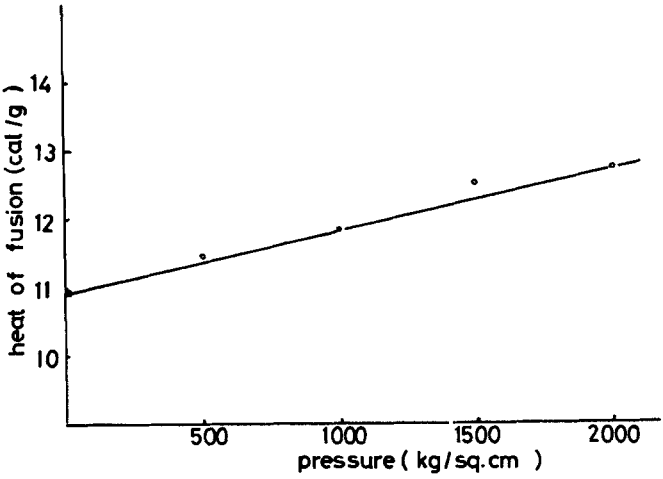

FIG. 6. Plots of heat of fusion of nylon 6 filaments drawn under pressure against pressure.

the fibers drawn at atmospheric pressure at 500 kg/cm^2, the 0,14,0 meridional reflection in the range 2θ = 75-82° shows a very small intensity, while the sample drawn at 2000 kg/cm^2 shows a very strong intensity and a clearly distinguished peak at 2θ = 77.8°. It corresponds to the previous observation that with increasing pressure, crystallinity and orientation are increased.

CONCLUSIONS

In drawn nylon 6 filaments at atmospheric pressure, there exist two crystal structures, the α- and γ-forms. With increasing pressure, however, structural conversion from the γ-pseudohexagonal to the α-monoclinic form occurs. Crystallinity and orientation are also increased with an increase of pressure.

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