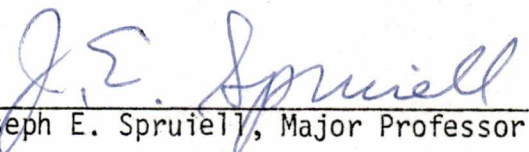
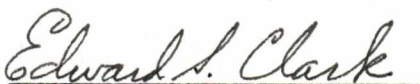


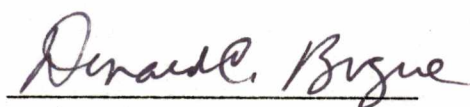
To the Graduate Council:

I am submitting herewith a thesis written by J. Gianchandani entitled "Structure Development in Fiber Formation of Nylon-6." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


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A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

J. Gianchandani

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ABSTRACT

A comprehensive study of structure development in fiber formation from nylon-6 was performed. A major emphasis of the research involved on-line birefringence measurements and studies of the development of orientation and crystallinity. The effects of annealing fibers in air, water and a 20 percent aqueous solution of formic acid were also studied. Tensile properties of as-spun and drawn fibers were measured and related to the spinning variables and structural characteristics.

The on-line structure development studies consisted of measuring changes in the birefringence as the filament crystallized on the bobbin in ambient atmosphere. Previous work has shown that nylon-6 filaments remain amorphous in the running spinline even at very high spin draw ratios. Subsequently, nylon-6 crystallizes in a pseudohexagonal form on the bobbin in the presence of moisture. Higher spin draw ratios (SDR's) result in higher crystallinity. A sample with a high γ content can be produced directly by melt spinning at high speeds. The total crystallinity and the different crystalline fractions have been analyzed by means of a new γ index.

It is observed that the c-axis crystalline orientation function of the filaments increased with take-up velocity and spinline stress. Increasing the take-up speed resulted in higher tensile strength and modulus. The elongation to break however decreased with increasing take-up speed or spin-line stress.

The α -monoclinic structure had been found to result from drawing and

annealing at elevated temperatures. The present study shows that drawing enhances the crystallinity of the filaments. Drawing to very high drawn ratios results in a higher α -content. On annealing the γ -pseudo-hexagonal structure converts to an α -monoclinic form. This rate of change is greatest when annealed in formic acid, but lowest in vacuum, while intermediate in water.

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CHAPTER I

INTRODUCTION

The generic name "nylon" has been adopted for designating polymers of the polyamide type. Polyamides are produced by reactions in which the linkage forming the main chain of the macromolecule occurs through the formation of amide groups. A simple method of nomenclature is commonly employed to designate the number of carbon atoms in the repeating units; for example, the polyamide made from caprolactam, which contains six carbons, is known as nylon-6. Further identification of the multiplicity of commercial nylons in world production may be found in the index to Man-Made Fibers (64).

Nylon-6 was the first important all synthetic fiber. The polymer is used mainly in the apparel, carpet and tire industry. Nylon-6 has been known for about 50 years and its worldwide commercial production is in excess of 2.2 million metric tons annually.

Most commercial operations for the production of nylon-6 fibers use the melt spinning process. The fibers are produced by extrusion of molten polymer through a die or a spinneret. The filament or multi-filament bundle is "taken up" at high speeds by a wind-up device. At this stage the fibers are said to be in their "as-spun" state.

In a second process known as "hot drawing", the as-spun fibers are delivered to a roller, passed through a heating device, a second roller, and a wind-up machine. The linear speed of the second roller is set at about 2 to 6 times that of the first and the heating device is adjusted to a temperature between T_g and T_m for the polymer. The fibers may further be annealed.

The melt spinning step involves crystallization or vitrification together with the formation of considerable molecular orientation. The spinning conditions determine the degree of molecular orientation. Previous experiments by Bankar (7) have shown that nylon-6 filaments are amorphous along the spinline. Development of crystallinity takes place on the bobbin. The development of crystallinity is affected by the humidity and temperature of the environment. The drawing and annealing processes (8, 73, 98) further enhance the crystallinity and orientation of the filaments.

In order to undertake the ultimate task of relating the end properties of the polymer to the process variables, an understanding of the morphology evolution as a function of processing variables is important. As one can deduce from the sequence of processes mentioned above, there are a large number of variables involved in the production of the final product. The entire sequence is important because the material tends to remember its processing history.

There is considerable discussion in the literature concerning the nature and stability of the various crystalline forms that this important polymer may assume. The purpose of this research is to survey the crystallinity and crystal structure data reported to date and to rationalize certain conflicting interpretations with additional measurements of our own. Analysis of the X-ray data by a newly formed γ -index provides a quantitative interpretation of the structural and morphological changes taking place.

This research is a continuation of work on fiber processing carried out in the Department of Chemical, Metallurgical and Polymer Engineering

at the University of Tennessee. The overall goal of this work is to provide a better understanding of the melt spinning, drawing and annealing processes, to relate processing variables to end use properties. The major emphasis of the research was to establish correlations between fibers with different processing histories by crystallinity, birefringence, density and mechanical property measurements. This work is a comprehensive study on the structure development and morphology of nylon-6.

CHAPTER II

LITERATURE SURVEY

General Background

Nylons belong to a general class of polyamides which are condensation products containing a recurring amide group NH-CO as an integral part of the main polymer chain. The first polyamide was synthesized by Gabriel and Maass (29). More than thirty years later, in 1929, this study was renewed by Carothers and Berchet at E. I. duPont de Nemours & Co. (14,15). This was part of their pioneering development of melt spinning. The first patent was applied for on June 13, 1931, and issued on February 16, 1936 as U. S. Patent 2,071,250.

Following the publication in the early 1930s of Carother's work in the field of polyamides and other polymers; Schlack, working at the Berlin Lichtenberg plant of I. G. Farbenindustrie A. G., synthesized polyamides from ϵ -caprolactam using acidic aminocaproic acid as a catalyst (90). The I. G. Farben group succeeded in commercially producing coarse nylon monofilaments under the trademark of Perluran in 1939 (58). Dupont began experimental production of nylon-66, in 1938. The first commercial nylon-66 plant began production on 14 December 1939. The first nylon-66 stockings were introduced to the public in May 1940, and were an immediate and outstanding success.

A small-scale production of continuous nylon-6 filaments in Germany started in 1940 at the Berlin Lichtenberg plant and at the I. G. Wolfen plant; large-scale production of nylon-6 was started in 1941 and at the Landsberg (Warthe) plant of I. G. Farbenindustrie. Both nylon-6 and nylon-66 were manufactured as continuous filaments at the Landsberg plant, in

cold water and then cut into small pellets. The extruded polycaprolactam contains up to about 10 percent monomer and other oligomers. The latter are removed by washing the polymer in boiling water. The pellets are then dried to less than 0.1 percent moisture by weight before spinning.

A critical factor in the control of the properties of nylon-6 is the control or elimination of oligomers formed during polymerization. Caprolactam is the major component (about 70 percent) of the extrable portion; the remaining 30 percent consists of roughly equal portions of cyclic dimers, trimers, tetramers, pentamers, hexamers and highly cyclic oligomers (20).

Moisture Absorption

The ability to absorb moisture is an important factor in the ability of a fiber to adsorb dyes and to be dyed at normal pressures, as well as in its comfort in wearing. The static properties of nylon are considerably altered with an increase in moisture content. The static charges of nylon are highest under conditions of low humidity and low moisture absorption.

In the case of nylon-6, there is a significant decrease in the moisture absorption with increase in crystallinity (27). The moisture absorption is proportional to the amide groups per 100 atoms in the chain. In the case of nylon-6 three molecules of water are absorbed on two neighboring amide groups in an accessible region, i.e. the amorphous regions of the polyamide. The first molecule forms a double hydrogen bond between the carbonyl groups (firmly bound water) and the other two molecules form hydrogen bonds between the CO and NH groups (loosely bound water). Nuclear magnetic resonance indicates that there are two characteristic types of

sorbed water in nylon-6, and that the water molecules are comparatively immobile at water content below 4 percent, and very mobile at water content above 4 percent (50). It is further suggested that there is a third sorption state of water below 2 percent, which would correspond to a single monolayer of water in the polymer.

The chemical stability of nylon-6 is unaffected by water at ordinary temperatures, but at high temperatures, in the presence of moisture, hydrolysis and degradation occurs. Nylon-6 melts at $215-220^{\circ}\text{C}$, depending on its molecular weight. It is soluble in some acids and organic solvents. It is quite stable in alkaline solutions, but decomposes in the presence of acids.

Structural Forms of Nylon-6

Nylon-6 is essentially a linear molecule with a repeat unit. During crystallization from the melt the chains come together to form hydrogen bonds between carbonyl and amine groups. Infrared studies (69) on inter-chain distance show these bonds to have a typical length of $4.8 \text{ \AA}$.

Studies on the crystal structure of nylon-6 were first carried out by Brill (12). This was followed by a more precise analyses of the unit cell by Wallner (104). Later Holmes, Bunn, and Smith (38) reported the most complete crystal structure study. They proposed a monoclinic unit cell for nylon-6 with dimensions

$$\begin{array}{lll} a = 9.56 \text{ \AA} & & \\ \text{fiber axis } b = 17.24 \text{ \AA} & \text{angle } \beta = 67.5^{\circ} & \\ c = 8.01 \text{ \AA} & & \end{array}$$

All of these above authors recognized the existence of more than one crystalline form of nylon-6. Holmes et al. (38) proposed the name " β " for

the secondary structure that they observed. They also suggested that the " β " structure consisted of a staggered array of hydrogen bonded sheets.

In 1959, Ziabicki (119) proposed that the β structure was hexagonal. He reported in his paper that the β structure was predominant when nylon-6 is rapidly quenched from a melt into a dry atmosphere. He also observed that the β structure was unstable and could be transformed readily to an α structure by annealing or exposure to moisture. According to Kinoshita (54), there exists a basically different crystal structure which he called a " γ " structure. This γ structure is characterized by a twisted amide group which causes a shortening of the chain. He suggested that nylon-6 would remain in this structure after treatment with iodine-potassium iodide solution and washing with sodium thiosulfate solution. Wide angle X-ray (WAXS) data from quenched nylon-6 film is reported by Sandeman and Keller (88).

Ziabicki and Kedierska (120) studied melt spun, undrawn, nylon-6 filaments. They observed a poorly formed crystalline structure represented by a broad equatorial reflection corresponding to an inter planar spacing of $4.2 \text{ \AA}$ and a meridional reflection at $8.3 \text{ \AA}$. Cold drawing or hot water treatment yielded the Holmes-Bunn-Smith monoclinic structure, commonly known as the α -form. Reichle and Prietzche (78) published their work in 1962 which described a monoclinic structure (β form) as having opposed amide groups in adjacent hydrogen-bonded sheets. The above β form had earlier been identified by Bunn (38) and called the γ hexagonal structure. The crystalline form of melt spun fibers was later identified by Vogelsong (102) as being the same as the second phase observed in drawn fibers. He also published a paper (103) about crystal structure deter-

mination of nylon-6 fiber which has been treated with iodine. His conclusion was that the structure is hexagonal with statistically distributed hydrogen bonds in all three principal directions. In 1963, Roldan and Kaufman (80) summarized a series of studies by proposing that nylon-6 could exist as an " α " crystal (Homes, et al.), an " α paracrystal" (Brill) with variable unit cell parameters, a stable " β " crystal with a hexagonal structure (in drawn fibers) and an unstable pseudo-hexagonal structure similar to a nematic liquid crystal which they called the " γ " crystal (Ziabicki-Kedzierska). A series of papers have been published (5, 51, 100, 100) describing the transition between the α and the γ crystal by iodine potassium iodine treatment. According to some authors the γ crystal was hexagonal or pseudo-hexagonal (61); according to others it was monoclinic (314). None of the authors admitted the presence of a β structure as noted previously by Bunn, Reichle and Ziabicki. Later Illers (42) adopted a symbol " γ^* " to describe the hexagonal structure which yielded the structure on annealing. He thus distinguished his γ^* structure from the hexagonal structure which annealed to the monoclinic γ crystal of Arimoto (6); or the orthorhombic structure of Bradbury and Elliot (10, 11). Parker and Lindenmeyer (73) have summarized the unit cell data (converted to monoclinic form) for nylon-6. They observe that the reported unit cells fall into two classes: (1) in which the chain axis (b-axis) is in excess of $17 \text{ \AA}$ and the crystallographic β angle is 60° or greater, and (2) in which the b-axis is about $16.8 \text{ \AA}$ and the β angle is 60° or less. Hence there exist at least two basically different ways of packing nylon-6 chains into crystal structure; one in which the hydrogen bonds are between antiparallel chains which are almost completely extended and the fiber repeat distance

is $17 \text{ \AA}$; and the other in which the amide groups are twisted out of the plane of the methylene groups, shortening the chain repeat distance to about $16.8 \text{ \AA}$ and permitting hydrogen bonds to form between parallel chains.

Over the past decade, a number of attempts have been made to provide a means for quantifying the wide range of WAXS patterns obtainable from nylon-6. Attempts have also been made to rationalize the vast amount of data in the literature concerning the quantitative analysis of nylon-6 by wide angle X-ray diffraction (WAXS) is often confusing, contradictory and fragmented. This stems apparently from disagreements concerning the nature and nomenclature of the different crystalline forms present. The magnitude and perplexity of this problem is reviewed by Parker and Lindenmeyer (73). A reasonable rationalization is that there exist only two basic crystallographic forms α and γ (63, 64), but each can exist with various degrees of imperfection (paracrystallinity). Numerous attempts to measure the relative amounts of α, γ and amorphous nylon-6 present in a given sample have met with only limited success. The method of Roldan, Rahl and Patterson (79) assumes the existence of a β phase. Kyotani and Mitsuhashi (59) use peak heights and not areas to calculate the relative amounts of different crystal phases. Their method is hence influenced by the crystallite size and perfection, and will be subject to errors if the peak widths differ in different samples.

The crystallization perfection index of Dismore and Statton (23), originally employed for nylon-66 could be applied to nylon-6 and would involve a calculation of the separation of the (200) and (002, 202) maxima and is therefore limited to samples where the maxima can be easily resolved, e.g., in a fairly well developed α structure. Huismann, Heuvel

and Lind (40) have presented a mathematical model for separation of the two crystal structures. Three curves, assumed to represent the α and γ equatorial diffraction, are fitted by computer to the equatorial diffraction scans. However, an apparent limitation of this method is that the γ and amorphous contributions are treated as one of the three curves.

Stepaniak, Garton, Carlsson and Wiles (99) used a different approach in their analysis of crystal structure. They obtained an amorphous "template" by scanning the azimuthal intensity distribution of a highly oriented sample. Hence, a total crystalline contribution of a specimen was obtained by then subtracting the amorphous intensity from the overall intensity. They assume that the 200 and 202/002 reflections of the α form occur at $2\theta = 20^\circ$ and 24° respectively. Hence, all the crystalline scatter in the range of $2\theta = 18 - 20^\circ$ and above 24° results from the α form. The rest of the crystalline scattering is part α and part γ . Also, a pure (3, 4) diffraction pattern could be constructed in a pattern similar in shape and position to a highly developed γ structure (I-KI treated) or a very fast spun sample.)

Crystalline Orientation

General. Measurements of crystalline orientation is an important tool for studying fiber forming operations. The degree of crystal orientation in a fiber affects its mechanical and optical properties. Drawing enhances the tensile strength of a fiber and increases its orientation along the machine direction. Hermans (37) has defined a coefficient of axial orientation. Ziabicki (118) defines it as "a ratio of the resultant polarization anisotropy of a given fibrous system to the theoretical polarization anisotropy of the system consisting of ideally extended and axially paral-

1el macromolecules where the adding up of constituent polarization anisotropies of the individual structural elements is carried out geometrically, exclusively, neglecting the possible changes of internal field."

Mathematically it may be written as

$$f = \frac{(\alpha_{11} - \alpha_1)}{\alpha_1 - \alpha_2} \dots\dots\dots 1$$

For rigid crystallites, Hermans has shown, using a "Polanyi's sphere" construction that (37)

$$f = 1 - \frac{3 \overline{\sin^2 \phi}}{2} = \frac{3 \overline{\cos \phi} - 1}{2} \dots\dots\dots 2$$

where $\overline{\sin^2 \phi}$ and $\overline{\cos^2 \phi}$ are the average sine and consine squared values of the angle ϕ between the reference direction and the chain direction. The value of f is 0, 1 and -1/2 for random orientation, orientation parallel to the reference direction, or orientation perpendicular to the reference direction respectively.

Stein and Norris (97) and Stein (96) have used the above equations for calculating the orientation function of polyethylene crystals. They have defined (97) orientation factors for the a- and b- axes as well as the c-axis (chain direction).

It is sometimes important to determine orientation functions for all three crystallographic axes. This helps in the analysis of the total orientation and morphology of the sample. For cubic, tegragonal or orthorhombic crystal systems, all the three crystallographic axes are mutually perpendicular and the orthogonality relationship exists -

$$\overline{\cos^2 \phi_a} + \overline{\cos^2 \phi_b} + \overline{\cos^2 \phi_c} = 1 \dots 3$$

where ϕ_a , ϕ_b , and ϕ_c are the angles the three axes make with the reference direction. Hence

$$f_a + f_b + f_c = 0 \quad \dots 4$$

In such orthogonal crystal systems only two of the three orientation functions are independent. Therefore we need only two orientation functions to characterize the orientation of the whole system.

The $\overline{\cos^2 \phi}$ values required to determine an orientation function can be obtained from WAXS intensity measurements. To determine $\overline{\cos^2 \phi_a}$, we need the azimuthal distribution of the intensity of X-rays diffracted from the set of planes which are perpendicular to the a-axis i.e., h00 planes

$$\overline{\cos^2 \phi_a} = \frac{\int_0^{\pi/2} \overline{I_{h00}} \cos^2 \phi_a \sin \phi_a d\phi_a}{\int_0^{\pi/2} \overline{I_{h00}} \sin \phi_a d\phi_a} \dots\dots\dots 5$$

Wilchinsky (112) generalizes the analysis of orientation functions to non-orthogonal unit cells. The analysis could be used to determine the orientation function of a certain crystallographic axis even when reflections from the set of planes which are perpendicular to this axis are not available. This analysis has been used by Wilchinsky (111) and Hoshino et al. (39) and Samuels (87) to obtain the orientation functions of polypropylene films. The application of Wilchinsky's analysis of nylon-6 melt spun fibers will be discussed later.

Nylon-6. A number of papers have been published on the quantitative determination of crystalline orientation functions of nylon-6. Sakoku, Marosoff and Peterlin (82) reported data on chain axis orientation of nylon-6 bristles. They made use of Wilchinsky's analysis for (200), (002) and (202) reflections of monoclinic nylon-6 crystals. They report that

the chain axis orientation factor increased from 0.83 to 0.97 when the draw ratio of nylon was increased from 2 to 4.95. Most of their samples were drawn and annealed and hence had a high α content. Unfortunately they do not elaborate the assumptions involved in their calculations.

The absence of suitable meridional reflections in the monoclinic α form of nylon-6 makes the estimation of crystalline orientation difficult. Dumbleton, Buchanan and Bowles (24) used the (1) reflection in nylon-66 which occurs at $2\theta = 77^\circ$ and assumed the normal to this plane to be coincident with the chain axis (an error of 2°). This enabled them to approximate values of Hermans-Stein crystalline orientation functions (f) for their hot drawn samples. A similar approach could be used for nylon-6. Also f_a and f_c may be calculated according to the method of Inoue and Hoshino (43). Orientation functions f_a and f_c may be calculated for nylon-6 from the (200) and (002, 202) reflections of the α form; and f_b corresponding to the orientation of the crystalline chains may be calculated assuming the unit cell to be orthogonal and not monoclinic.

A semi-quantitative index of orientation may be calculated using the width at half height of the azimuthal intensity distribution of a selected reflection (77).

More recently Stepaniak, Garton, Carlsson and Wiles (98, 99) have used Wilchinsky's (110) analysis to calculate orientations of the monoclinic α phase using the crystallographic data of Holmes, Bunn and Smith (38). They also calculated the orientation functions of the γ form by assuming true hexagonal symmetry. Hence the Hermans-Stein orientation functions for the γ -form were calculated from the equatorial reflection and Wilchinsky's relation -

$$2f_a = 2f_b = -f_c \quad . . . 6$$

where f_c is chain orientation. They report an increase in the chain axis orientation from 0.22 to 0.80 by drawing up to 4.5X at room temperature.

Morphology Developed by Quiescent Crystallization

Single crystals of nylon-6 have been obtained by Geil (30) by precipitating nylon-6 from a glycerine solution. The thickness of these single crystal lamellae was about $60 \text{ \AA}$. Ogawa et al (60) reported that the diffraction pattern of nylon-6 single crystals correspond to the γ pseudohexagonal form. Geil (30) observed that both positively and negatively birefringent spherulites were formed along with single crystals in the same solution.

Spherulites structure was also observed in melt crystallized nylon-6 by Magill (62) and Inoue (44). The diameters of the spherulites varied between 10-50 μ depending on the temperature of crystallization.

Crystallization Kinetics

Experimental observations of the development of crystallinity in polymers are of many types. In one case a property varying with the total amount of crystallinity, such as specific volume, is observed as a function of time at constant temperature. Alternatively the rate of formation and growth spherulites is observed directly with the microscope. The two techniques lead essentially to the same results. Crystallization rates have also been measured using X-ray, infrared, and density techniques.

The crystallization rate is analyzed by the well-known Avrami equation, which gives rate constants and crystallization mechanisms. However,

many experiments show that the equation cannot describe the overall process of the polymer, the perfection of crystals and a slow growth of crystallite size resulting from the stress relaxation or entanglements might occur. Furthermore, in some cases the primary and secondary crystallization processes overlap. (81)

Many workers have measured the rate of growth of spherulites of nylon-6 and 66 (6, 13, 16, 45). Some authors have reported the crystallization kinetics of nylon-6 with respect to the temperature change and density change of the specimens during the crystallization process. The rate constants were calculated by use of the Avrami equation:

$$a = a_{\infty} (1 - e^{-kt^n})$$

Where a and a_{∞} are crystallinity at time t and infinity respectively. K is a rate constant and n is a constant depending on the mechanism of nucleation and growth of crystals.

Burnett and McDevit (13) have studied the growth of nylon-6 spherulites in a temperature range of 102°C to 182°C. They plotted the rate of growth vs temperature and obtained a typical bell-shaped curve. They observed that at constant temperature the growth rate was a constant. Inoue (45) obtained crystallization isotherms of nylon-6 at temperatures from 205°C to 215°C using a dilatometric technique. The avrami equation was used to calculate the half times of crystallization, $t_{1/2}$. The half time was found to be 18 minutes or higher depending on the crystallization temperature. The rate of crystallization was found to be lower for polymers of high molecular weight. Later (44) he studied the effects of various nucleating agents on the rates of crystallization. The use of nucle-

ating agents resulted in decrease of induction time and increase in the rate of crystallization.

Magill (62) studied the effects of melt history, moisture content and relative viscosity on induction time during isothermal crystallization. He also measured the kinetics of isothermal crystallization over a wide range of temperature using an on-line camera and depolarized light (63). He observed the maximum rate of crystallization to occur at around 140°C. At that temperature the half time of crystallization was ten seconds. The half time increased for higher crystallization temperatures. The kinetics of strain induced crystallization of nylon-6 has not been the subject of any published work so far.

Structure Development During Melt Spinning

General. As early as 1932, Carothers and Hill (14) noted the effects of spinning variables such as fiber tension on the X-ray diffraction patterns of polyamides and polyesters. They observed evidence of molecular orientation. Keller (53) in 1956 discussed qualitatively the orientation and crystallinity in melt spun fibers. He reported X-ray data from nylons, polyethylene and polyethylene terephthalate. Later Hearle (36) investigated the crystalline structure of fibers but did not deal with the spinning processes as such. Ziabicki (116, 117, 120) used birefringence and X-ray diffraction to study the effects of spinning parameters on the molecular orientation of nylon-6 fibers. He reported that the orientation of molecules increased with spin-line stress, parallel velocity gradient and inverse of fiber diameter (measure of cooling rate). Abbot and White (1) studied melt spinning of low and high density polyethylene and examined

variation of orientation and crystallinity in the spun fibers with spinline stress, melt flow rate and melt temperature. The modulus and tensile strength of the fibers increased with increasing crystalline orientation.

The crystallization process in the melt spinning of nylon-66 fiber was studied by Chappel and co-workers (17). They observed the effect of moisture on the crystalline character of the polymer using techniques such as X-ray diffraction, depolarized light and microscopy. Katayama, Amano and Nakamura (52) used similar techniques to study the structure development during melt spinning of polyolefin fibers.

A number of researchers have made on-line WAXS measurements on a fiber spinline including Chappel et al. (17), Katayama, Amano and Nakamura (52), Dees and Spruiell (21), Nadella, Henson, Spruiell and White (72), Bankar Spruiell and White (7). Recently Spruiell and White (94) have reviewed studies of structure development in fiber formation from aliphatic polyamides and polypeptides.

Nylon-6. Among the earliest of the basic studies of structure development during melt spinning are those of Ziabicki and Kedzierska (116, 120). They studied the WAXS patterns and birefringence of spun fibers and correlated the birefringence with an increasing function of spinline stress. Hamana, Matsui and Kato (32) and Ishibashi, Aoki and Ishii (48) made on-line measurements of birefringence and determined Δn as a function of spinline position. The latter also reported a time dependent increase in birefringence of as spun yarn if placed in a 50 percent relative humidity environment.

Ishibashi and Ishii (47) have also investigated the effect of heating

chambers placed around the spinline on the birefringence of the running filament. They suggest that the increase in birefringence is due to crystallization of the filament. Studies of melt spun nylon-6 fibers have also been published by Pasika, West and Thruston (74), Sakoaku, Morosoff and Peterlin (82), Wasiak and Ziabicki (107). Recently Bankar et al. (7) made on line WAXS and birefringence measurements on a nylon-6 fiber spinline. Spinning was carried out in air at 65 percent relative humidity. The WAXS pattern obtained was a diffuse halo even at high spinning speeds of about 1000 m/min. Hence they concluded that the as-spun fiber is amorphous and that the crystallization of nylon-6 takes place on the bobbin. They also measured the birefringence of the running filaments along the spinline. The birefringence of the filaments increased gradually with distance from the spinneret. The birefringence also increased with take-up velocity or take-up stress.

Structure development in wet spinning of nylon-6 has been studied by Kiyotosukuri, Hasegawa and Imamura (57) and by Hancock, Spruiell and White (33). The authors report that in most cases wet spun fibers exhibited the α -monoclinic crystal structure.

Nylon-6 in the pseudo-hexagonal γ -form is produced when the melt is rapidly quenched (7). The pseudo-hexagonal form may be converted to the monoclinic α form by annealing or by drawing (38). Spinning at high speeds (i.e., at high extrusion and take-up rates) produced an oriented γ form. The α form may be converted into the γ form by treatment in an aqueous solution of iodine and potassium iodide (6, 33, 62). The γ form obtained either by high speed spinning or iodine treatment cannot be wholly reconverted to the α form by conventional annealing.

Post Treatment of Spun Fibers

Post treatment of spun fibers may include drawing, annealing, twisting, etc. The processes of annealing and drawing as applied to nylon-6 will be treated in this section.

Annealing. Annealing is heating of the polymer without any melting or large scale deformation. Annealing affects the structural characteristics of the fiber. Annealing causes changes in crystal thickness and shape, chain conformation and promotes secondary crystallization.

Studies on the polymorphic phase changes in nylon-6 fibers due to annealing have been carried out by Banker (7), Stepaniak et al. (98) and Parker and Lindenmeyer (73), Sandeman and Keller (88).

When a quenched film of nylon-6 was annealed at various temperatures, Sandeman and Keller (88) observed that annealing causes a gradual change from a pseudo-hexagonal form to a monoclinic form. Banker (7) observed that when as-spun and conditioned fibers are annealed in air, water or a 20 percent formic acid solution, the pseudohexagonal structure changes into a monoclinic structure. The change is more rapid and the α -phase produced is more perfect when annealed in formic acid. Water is slightly less effective in promoting this change than formic acid. Similar results have also been reported by Parker and Lindenmeyer (73) who obtained X-ray diffractometer scans of nylon-6 fibers annealed at series of different temperatures.

Stepaniak et al. (98) report that when as-spun and conditioned filaments are annealed in vacuum, the γ to α conversion occurs only at temperatures greater than 120°C. At lower annealing temperatures both the α and γ crystalline phases increase slightly with annealing.

Tsuruda (100) has shown that the crystallinity and long period of nylon-6 increases with dry heat setting and especially steam setting. He reported that the WAXS intensity increased with steam setting. Bankar et al. (7) also observed the long period of spun filaments to increase with annealing temperature.

Drawn Fibers. Drawing of the melt spun fibers greatly increases the modulus and tensile strength but decreases elongation to break. White, Dharod and Clark (108) studied drawn polyethylene fibers and reported that the tensile strength and modulus increased by a factor of about ten over the melt spun fiber. They also proposed a structural model for the drawn polyethylene fibers.

Samuels (84) has done studies on drawn polypropylenes. According to him the average state of orientation of the polymer is a useful expression for comparing structure-property relationships. Average molecular orientation is defined as

$$f_{av} = X f_c + (1 - X) f_{am}$$

The drawing of nylon-6 has been studied by Stepaniak et al. (98) who reports that drawing of as-spun and conditioned filaments results in an appreciable increase in the overall crystallinity. This effect increases with increasing draw ratio. An α - γ mixed component structure is retained at low draw temperatures but a predominantly α form is produced at high draw temperatures. The crystalline orientation of the fibers maximized at an oven draw temperature of 130-155°C. Parker and Lindenmeyer (73) have also reported studies on drawn fibers. A major drawback of their

study is that their fibers are commercial nylon-6 fibers and they have not mentioned the spinning and drawing particulars.

CHAPTER III

EXPERIMENTAL DETAILS

A. MATERIAL

General Characteristics

The polymer used in this study was a commercial grade nylon-6, courtesy of the American Enka Company. The polymer was received in the form of cylindrical pellets. The pellets had an average length of 3 mm and an average diameter of 2 mm.

The average density of the pellets was 1.16 g/cc. The pellets were undried and had a moisture content of 0.34 percent. Before using this sample for any experiments, it was dried in a laboratory vacuum oven at 110°C. The characteristics of this sample were supplied by the American Enka Company and are listed in Table 1. The relative viscosity of the sample was obtained for a solution of one percent nylon in 90 percent formic acid at 20°C. The number average and weight average molecular weights were obtained from GPC.

Drying of Nylon

The drying was carried out in a laboratory type vacuum oven model 5831, manufactured by National Appliance Company, Portland, Oregon. The drying of the polymer was carried out in batches of 1500 gms under an absolute pressure of 0.5 inches of mercury at 110°C.

The sample was dried for 16 hours and then allowed to cool to room temperature in vacuum. The moisture content was brought down to 0.03 - 0.04 percent. After drying the samples were stored in glass jars. This

TABLE I
CHARACTERISTICS OF NYLON-6 SAMPLE

Sample	Moisture Percent	Relative Viscosity	End Groups		M_n	M_w	$\frac{M_w}{M_n}$
			Million NH_2	gms COOH			
Undried	0.34	2.45	54	39	7,600	36,200	4.77
Dried	0.076	2.65	29	49	22,500	46,900	2.08

nylon drying procedure has earlier been used and found satisfactory by Bankar (8).

B. MELT SPINNING EXPERIMENTS

The extrusion of nylon-6 was carried out in both the Instron Capillary Rheometer and in a Modern Plastics Screw Extruder. Extrusion in the capillary rheometer was used to obtain fibers at different take-up velocities and to conduct on-line birefringence experiments. The screw extruder provided a means for obtaining filaments produced under steady state conditions and very high take up velocities.

Instron Capillary Rheometer

The instron capillary rheometer is a ram extrusion apparatus with a motor driven piston. The piston moves at a constant velocity and the piston force is measured by a load cell and recorder. The load cell used was capable of recording up to 1000 pounds force and is mounted on a moving crosshead. Twenty different crosshead speeds (SHX) ranging from 0.02 inch per minute to 20 inches per minute may be selected. The piston assembly is electrically heated to preselected temperatures between 60 and 300°C with temperature control within 1°C and a constant temperature profile across the barrel.

The barrel is a 3/8 inch diameter, stainless steel pipe. It is about 20 inches long. The polymer is loaded from the top of the barrel. The die is fitted to the bottom of the barrel by means of a threaded cap. The Instron rheometer was used at 230°C. The die used had a diameter of 0.762 mm and an L/D ratio of 20. Figure 3.1 shows the spinning process.

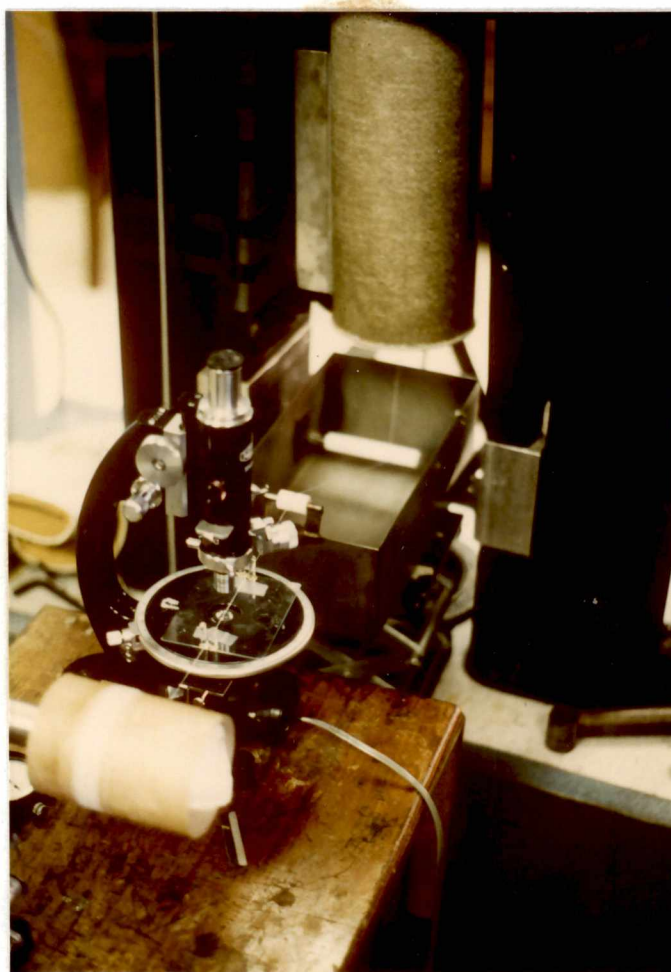


Figure 3.1. Experimental Set-Up for On-line Birefringence Measurements

Modern Plastics Screw Extruder

The MP screw extruder (hereinafter referred to as the extruder) was first used in our laboratory by G. E. Hagler (31). Figure 3.2 is a schematic diagram of the extruder. Details, modifications and operating instructions for the extruder are given in (9). All the experiments with nylon-6 were conducted at a melt temperature of 262°C . The filaments were spun at speeds 96, 480, 960, 1450, 1930 and 2410 meters per minute. The die used had a diameter of 0.762 mm and an L/D ratio of 10. During these runs the mass flow rate was kept at approximately 5.67 gms/min and the spinning medium was ambient air at 21°C . The spin path length was about 10 feet.

Birefringence Measurements

On-line birefringence measurements were carried out on the Instron rheometer spun samples. The birefringence of the running filament was measured using an Olympus polarizing microscope, Model POS with a Berek compensator. (see Figure 3.1)

The birefringence was calculated by dividing the measured retardation by fiber diameter. The diameters of fibers were measured with a Bausch and Lomb filar micrometer eyepiece. The compensator constant required for calculating the retardation was obtained by using two test plates of known retardation and then using the average of the two constants. The two plates used were a one-fourth wave length plate (mica, retardation = $147.3\mu\text{m}$) and a one-half wave length plate (gypsum, retardation = $530\mu\text{m}$). The compensator constant for the Berek compensator was found to be $C/10000$ equal to 0.895.

On-line birefringence measurements were used to study the crystal-

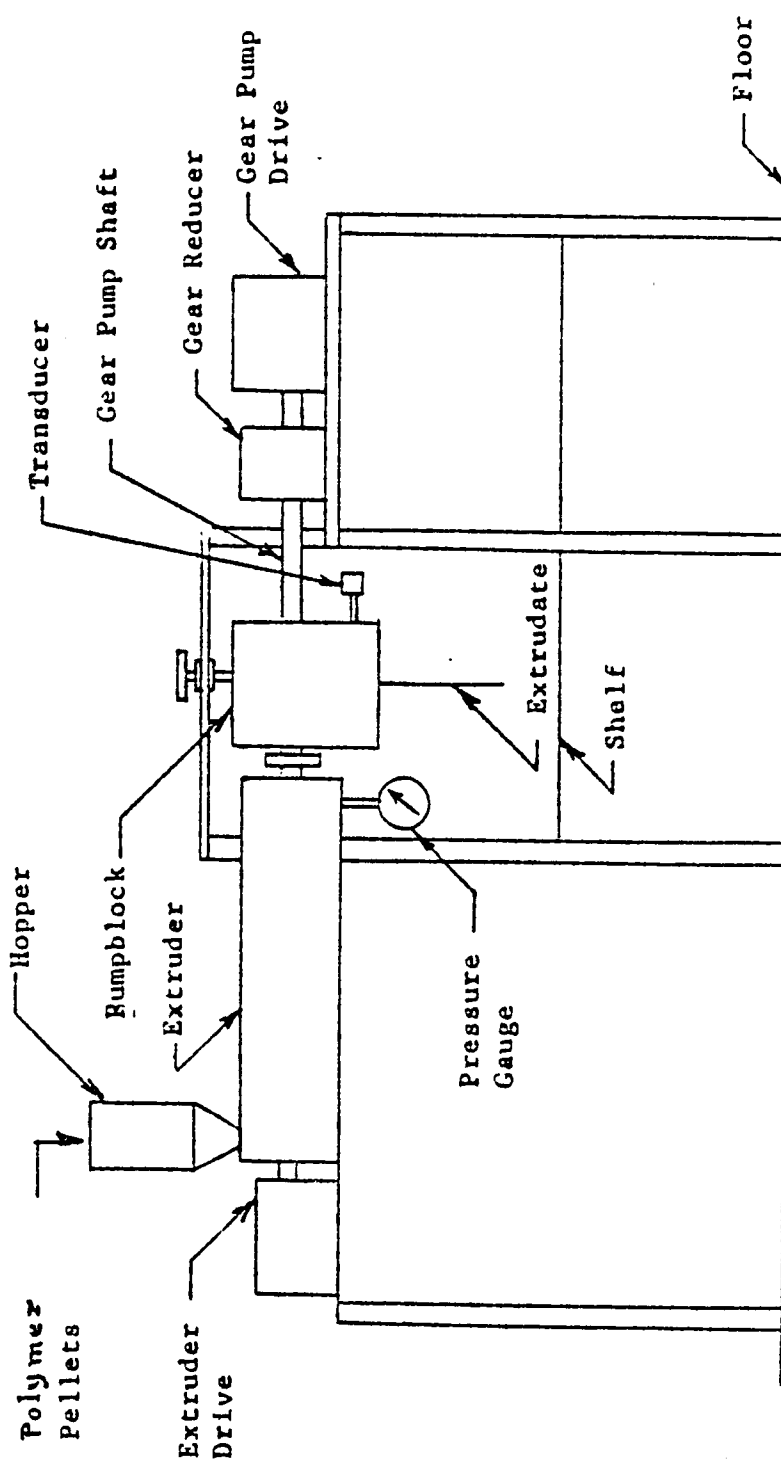


Figure 3.2. Schematic Diagram for Extrusion Apparatus

Source: G. E. Hagler, Ph.D. Dissertation in Chemical Engineering,
The University of Tennessee, Knoxville (1972).

lization kinetics of nylon-6. The rate constants were calculated by use of the Avrami equation:

$$\phi = \phi_{\infty} (1 - e^{-kt^n}) \dots \dots \dots (1)$$

where ϕ and ϕ_{∞} are crystallinity at time t and infinity respectively.

k is a rate constant and n is a constant depending on the mechanism of nucleation and growth of crystals. In birefringence studies we may rewrite equation 1 as

$$\frac{\phi_f - \phi_0}{\phi_f - \phi_c(t)} = \exp(kt^n) \dots \dots \dots 2$$

where ϕ_0 is initial crystallinity
 ϕ_f is final crystallinity
 ϕ_c is crystallinity at any time t

Equation 2 can be rewritten as eq (3) and (4);

$$\ln \left(\frac{\phi_f - \phi_0}{\phi_f - \phi_c(t)} \right) = kt^n \dots \dots \dots 3$$

$$\text{or } \pi = \ln \left[\ln \left(\frac{\phi_f - \phi_0}{\phi_f - \phi_c(t)} \right) \right] = \ln k + n \ln t \dots \dots \dots 4$$

The crystallinity value may be calculated from

$$\Delta = \phi_c f_c \Delta_c^0 = (1 - \phi_c) f_a \Delta_a^0 \dots \dots \dots 5$$

where

Δ is total measured birefringence
 Δ_a^0 is intrinsic birefringence in the amorphous phase
 Δ_c^0 is intrinsic birefringence in the crystalline phase
 f_c is orientation function of the crystalline phase
 f_a is orientation function of the amorphous phase

Equation (5) may be rewritten as:

$$\phi_c = \frac{\Delta - f_a \Delta_a^0}{f_c \Delta_c^0 - f_a \Delta_a^0} \text{-----} 6$$

For nylon-6, Δ_c^0 and Δ_a^0 have values .0963 and .0825 respectively (66).

For all practical purposes we assumed:

$$f_a \Delta_a^0 \approx \Delta_0$$

where Δ_0 is the birefringence in the amorphous sponline. Since all experiments started at the amorphous level ϕ_0 was assumed zero. ϕ_f was evaluated from the measured ϕ versus time curves as the percent crystallinity at ten times the half life. This procedure has been earlier used by Benaim (9), and by Spruiell and McCord (67, 95).

A mathematical relationship suggested by Schultz and Scott (91) in their study of secondary crystallization of linear polyethylene was used by Spruiell and McCord (67, 95) in their work on PET. In this research a similar analysis was used to interpret the portions of the crystallization. The percent crystallinity varies as a linear function with $\ln(t)$ at a rate defined by A:

$$\phi_t = A \ln(t) + B$$

C. EXPERIMENTAL MEASUREMENTS FOR CHARACTERIZATION OF SPUN AND DRAWN FILAMENTS

The structure of the spun filaments was characterized through density measurements, wide angle X-ray diffraction (WAXS) and birefringence studies. Density and WAXS were combined in order to estimate the relative amounts

of phases present. WAXS and birefringence measurements were used to study the orientation of the filaments.

Density

The techniques to make density gradient columns are discussed by Wiley (109) and are specified by the American Society of Testing Materials under the designation D-1505-68 (22).

A mixture of carbon tetrachloride and toluene was used to make solution A (heavy) and solution B (light). Two concentric cylinders, connected by a glass tube were used to facilitate the mixing of solution A and solution B. The density gradient column was kept at 23°C by means of circulating water. Five floats varying in densities from 1.10 to 1.15 gm/cm³ were used to standardize and calibrate the column. Density readings for different samples were obtained after the samples had stabilized in the column for at least 12 hours.

Wide Angle X-Ray Scattering (WAXS)

Wide angle X-ray diffraction flat plate film patterns for the samples (as spun, drawn annealed) were obtained using a Philips Norelco X-ray generator. The radiation used was Ni filtered Cu K_α of wavelength 1.542 Å. The X-ray unit was operated at 40 KV and 15 MA. The sample to film distance was 3.71 cm and the sample was fixed on a sample holder which was attached to the beam collimator by a rubber cap. Exposure time usually ranged from 20 minutes to one hour.

X-Ray Diffractometer Scans

An XRD-5 General Electric X-Ray Diffractometer was used to obtain the 2θ scan of the as-spun filaments as well as the treated fibers. Fibers

were wound on an H frame in a parallel alignment. A specially designed slit system was used to collimate the X-rays. This instrument was also used for the ~~axi~~^zimuthal scans needed for quantitative evaluation of orientation factors.

D. QUANTITATIVE ANALYSIS OF X-RAY PATTERNS

a) Approximate relative amounts of phases (γ index).

The diffraction patterns of various filaments (as-spun, fast spun, ϕ drawn and annealed) were analyzed using a new γ index based on WAXS area ratios in combination with density data. The ratio R was defined as the ratio of the area of the meridional 020 peak to the area of the equatorial reflection between 18-24°. The ratio R was used to establish the γ index. This γ index may be used to calculate the two crystalline fractions of nylon-6 (α and γ), the total crystalline fraction and the amorphous fraction. For this purpose two samples - one high in α content and the other high in γ content are prepared. The γ sample used had the highest γ content we could obtain and will be referred to as our standard γ sample. This standard γ sample was obtained by treating a fast spun sample (SDR=237.3) in warm potassium iodide solution for half an hour, followed by washing in cold sodium thiosulphate solution.

Our standard γ sample had a density of 1.1455 g/cm³, and a ratio $R_\gamma = 128.0 \times 10^{-2}$. Assuming the α content of this sample to be negligible, a crystalline fraction of 0.75 was determined using the standard relationship

$$X_\gamma = \frac{\rho_\gamma}{\rho} \left(\frac{\rho - \rho_{am}}{\rho_\gamma - \rho_{am}} \right) \text{ --- 8}$$

where

ρ_{γ} = theoretical density of phase γ

ρ_{am} = density of amorphous nylon-6

ρ = measured density of the sample

Our standard α form was obtained by hot drawing a low SDR (14.3) sample to 4X. The drawn sample was then boiled in a 20 percent aqueous solution of formic acid for half an hour. Our standard α sample had a density of 1.1575 g/cm³ and a ratio $R_{\alpha} = 1.11 \times 10^{-2}$.

We may now define the γ index as X_{γ} , the approximate volume fraction of the sample which is γ phase as:

$$X = \frac{R_s - R_{\alpha}}{R_{\gamma} - R_{\alpha}} \times 0.75 \quad \text{--- 9}$$

where $R = \frac{\text{Area I020}}{\text{Area under equatorial Peak 18-24}^{\circ}}$

and the factor 0.75 represents the crystallinity of the standard sample. Since

$$X_{\gamma} + X_{\alpha} + X_{am} = 1.0 \quad \text{--- 10}$$

and
$$V_s = X_{\gamma} V_{\gamma} + X_{\alpha} V_{\alpha} + X_{am} V_{am} \quad \text{--- 11}$$

where V_s = specific volume of the sample
 V_{γ} = specific volume of the γ phase
 V_{α} = specific volume of the α phase
 V_{am} = specific volume of amorphous phase.

equations (2) and (3) may be combined to give

$$X_{\alpha} = \frac{(V_s - V_{am}) - \frac{X_{\gamma}}{\alpha} (V_{\gamma} - V_{am})}{V_{\alpha} - V_{am}} \quad \text{--- 12}$$

Equations (1), (2) and (4) may now be used to obtain relative fractions of the crystalline and amorphous phases in the sample.

The specific volumes are obtained from the density data. For our calculation we used the following (27):

$$\text{density of } \alpha \text{ phase} = 1.23 \text{ g/cm}^3$$

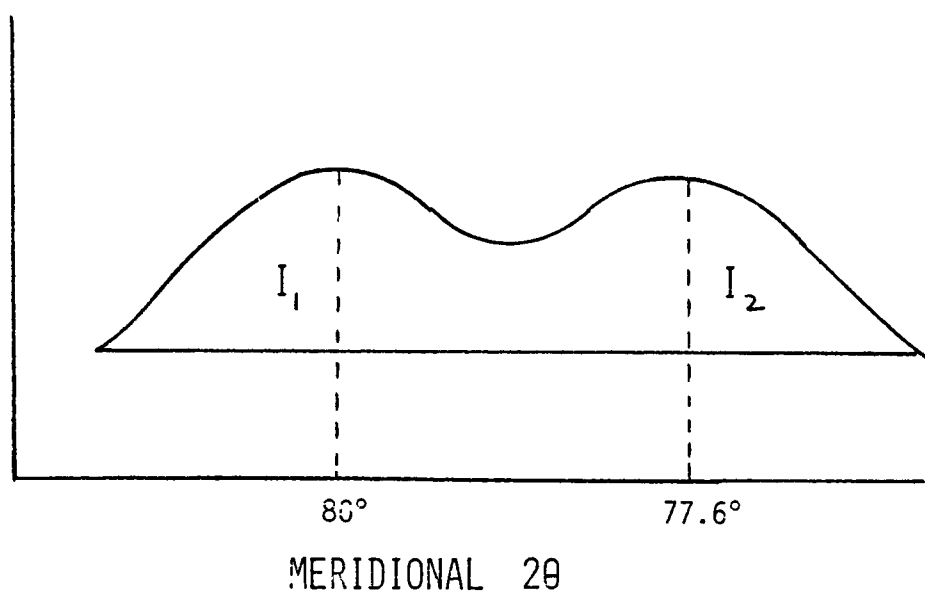
$$\text{density of } \gamma \text{ phase} = 1.17 \text{ g/cm}^3$$

$$\text{density of amorphous phase} = 1.08 \text{ g/cm}^3$$

The new indexing method is a reasonably rigorous approach to quantitative analysis of the relative amounts of phases. This method has the advantage of giving values for X_γ , X_α , X_{am} . There are certain assumptions made in this method. The integrated intensity of the meridional 020 reflection is assumed to result from the γ phase. The crystalline scatter in the range $2\theta = 18 - 24^\circ$ results from the α phase, the γ phase, plus all of the amorphous contributions. There is no correction factor for distorted α and γ unit cells in calculating the component indices as recommended by Parker and Lindenmeyer (73).

b) Characterization of nylon-6 filaments by analysis of 0, 14, 0 peak.

Parker and Lindenmeyer (73) have reported data on the 0, 14, 0 meridional reflection of nylon-6. The 0, 14, 0 reflection occurs around $77-80^\circ$ and represents the crystalline phase. The α peak occurs at 77.6° and γ peak at 80° . Using these data the γ fraction in the sample was estimated by dividing the area of the peak at 80° by the sum of the areas of the peaks at 80° and 77.6° . (see figure 3.3) This analysis was carried out for a particular sample with a SDR of 240. Additional calculations were not carried out due to lack of data. Therefore a thorough comparison of the two indices is not possible at this time. All the results obtained by using this method are presented in the Appendix.



$$\gamma \text{ FRACTION} = \frac{I_1}{I_1 + I_2}$$

Figure 3.3. Characterization of Nylon-6 Filaments by Analysis of the 0,14,0 Peak.

CHAPTER IV

STRUCTURE DEVELOPMENT IN MELT SPINNING

General

Previous studies by Bankar (7, 8) have shown that nylon-6 is amorphous on a running spinline and the development of crystallinity takes place on the bobbin. In the present work, it was decided to undertake on-line studies to bridge a gap between the work of Bankar (7, 8) and the final properties of the as-spun and conditioned fibers. It was considered essential to observe the development of crystallization to provide a thorough analysis of the primary and secondary stages. The Instron Rheometer with an on-line set up as explained in Chapter III was used for on-line measurements of birefringence. The advantage of the Instron over the screw extruder was that it provided us with slower and more manageable spinning speed but comparable SDR. Nylon-6 samples spun on the extruder, hereon referred to as the MPE samples were spun at much higher speeds. These samples had been earlier spun by another investigator to be used in the present analysis.

On-line Studies of Cold Crystallization

Results of On-line Measurements. Figure 4.1 shows the change in birefringence as the filament crystallizes in atmosphere at 55 percent RH and 60°F. The birefringence was measured as a function of time for a sample taken from the spinline near the bobbin. Data were obtained for a range of different SDR's ranging from 15 to 660. It was

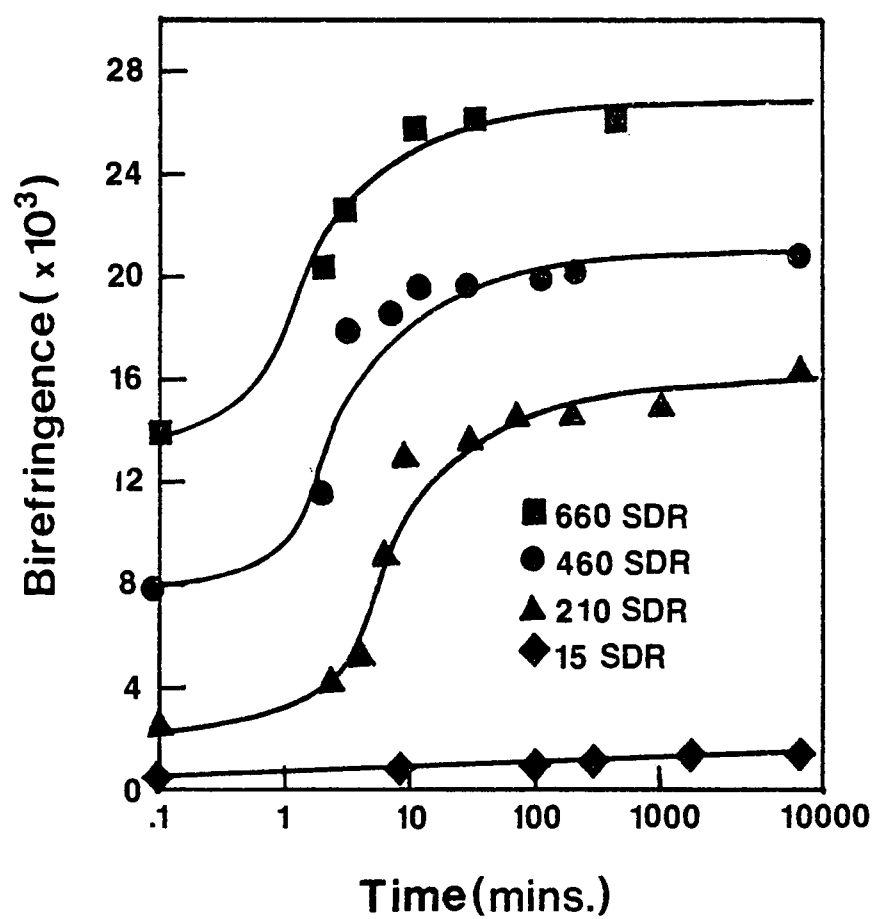


Figure 4.1. Birefringence of Melt Spun Nylon-6 as a Function of Time, at 55% RH and 60°F.

observed that the birefringence value is steady with time, then increases sharply until finally leveling off again. This results in characteristic S-shaped curves. In the range of SDR's, temperature and humidity studied the minimum time required for the beginning of the sharp rise was of order 0.5 to 1 minute. Thus the change would occur well after the filament would normally be wound on the bobbin. Equations III-5 to III-7 could be used to extract the crystallinity changes associated with the changes in birefringence. A plot of $\ln(\ln \phi)$ versus $\ln(t)$ for the samples crystallized in atmosphere (55 percent RH and 60°F) is presented in Figure 4.2. These samples were spun at three different SDR's namely 15, 210, 460, and 660. The process appears to occur in two stages, analogous to a primary and secondary crystallization. Table II shows the values of the Avrami constants for the primary crystallization process obtained from Figure 4.2 and equations as described in chapter III. Figure 4.3 shows the secondary crystallization process as described by equation III-7.

Discussion of On-line Measurements. In the melt spinning of nylon-6, the birefringence in the spinline steadily increases from zero in the melt near the spinneret to a steady value associated with the orientation produced in the process. The present results show that there is a subsequent rise in the birefringence as the material conditions at ambient temperature. This increase of birefringence appears to result from increasing crystallinity of the fiber. This process results in characteristic S shaped birefringence curves which can be interpreted in terms of a primary and secondary cold crystallization process. Samples spun at higher SDR's, i.e., faster spinning speeds, have higher initial orientation and exhibit higher

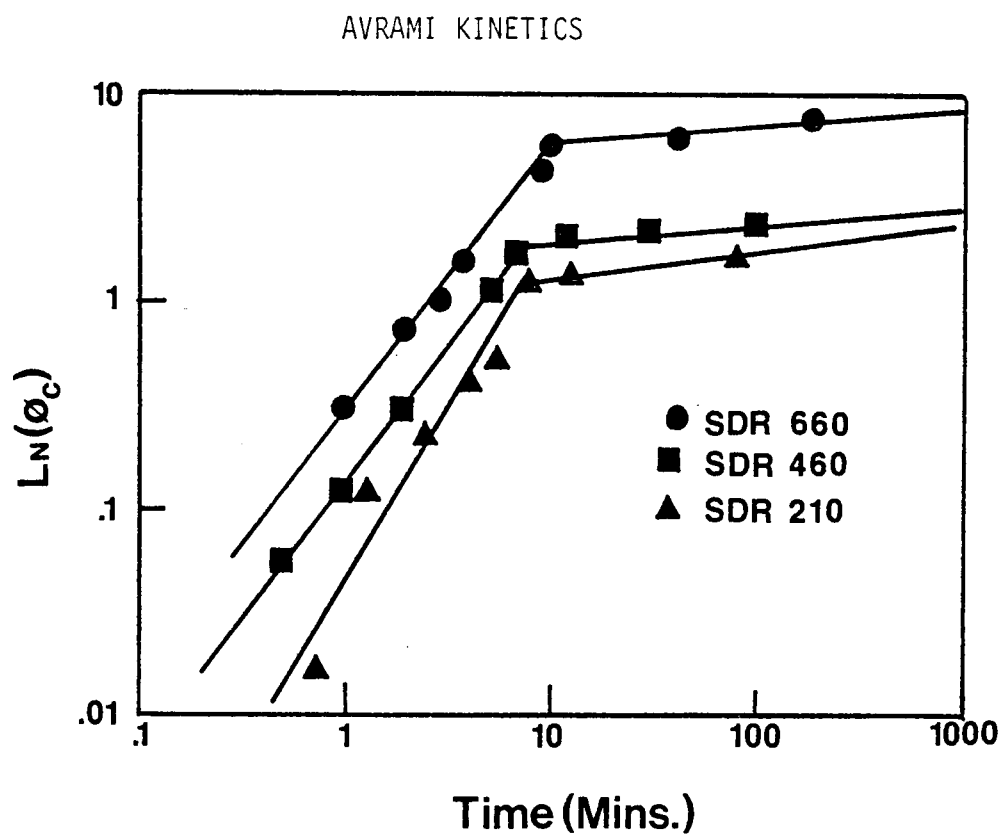


Figure 4.2. Avrami Plot for Crystallization Kinetics of Nylon-6.

TABLE II

AVRAMI CONSTANTS FOR INSTRON SAMPLES

SDR	N	K
660	1.34	0.012
460	1.4	0.0047
210	1.75	0.0008

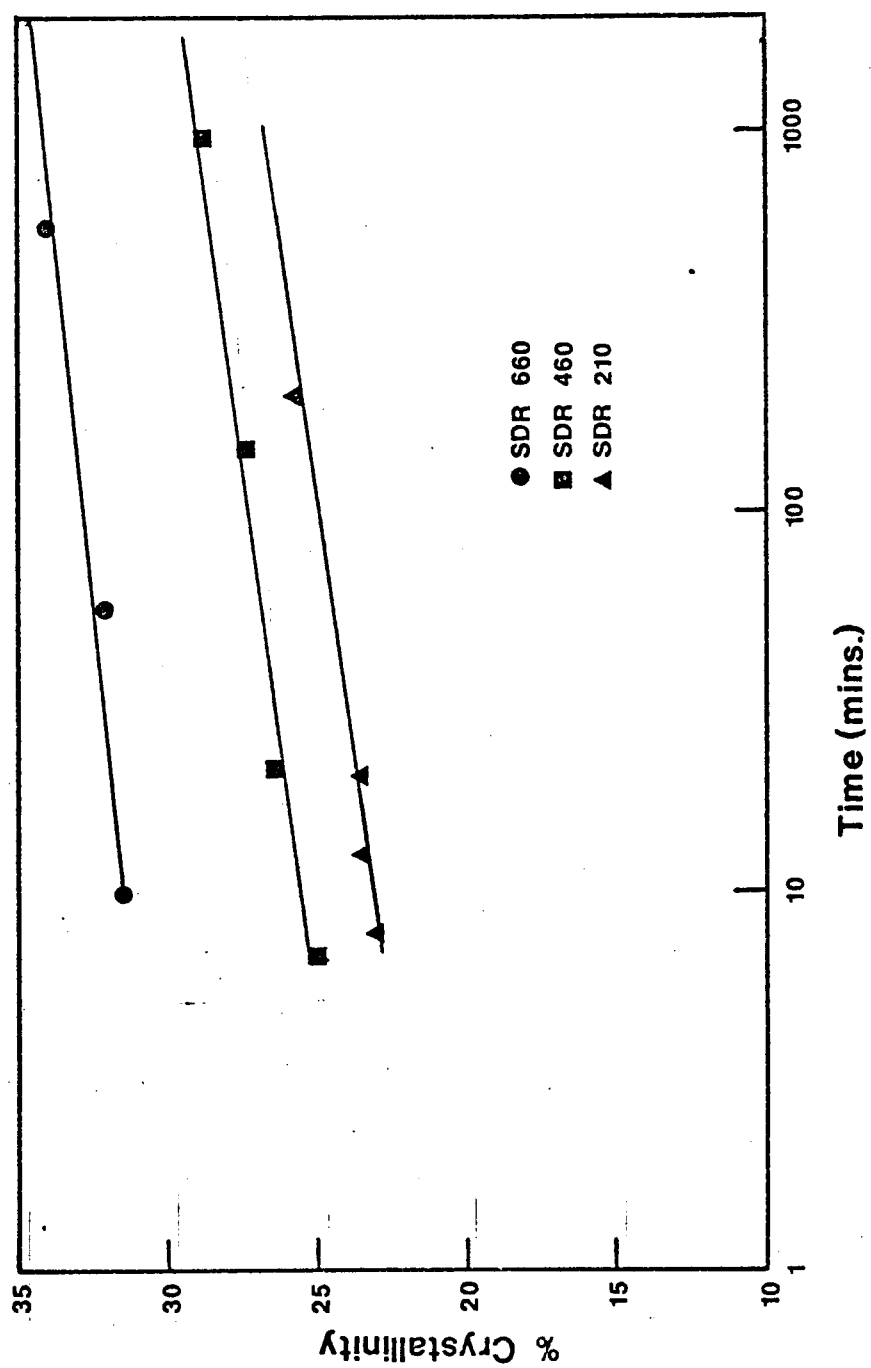


Figure 4.3. Secondary Crystallization of Nylon-6.

cold crystallization rates. As discussed more fully in a later section, it is believed that the cold crystallization results in the formation of pseudo-hexagonal crystallites. The formation of these crystallites coupled with crystallization induced orientation results in the large increases in birefringence. The marked increase in birefringence was not observed for samples with low SDR's. It is believed that this result is due to the inability to detect by birefringence any changes in the crystallinity that are not accompanied by increased orientation. On this basis low SDR's also are assumed to undergo cold crystallization, but the nearly random orientation of the crystallites precludes their detection by birefringence measurements. Thus it is possible to study the kinetics of cold crystallization only in the case of the high SDR samples and little can be said of the kinetics of cold crystallization in the low SDR samples.

The plot of $\ln(-\ln \phi)$ versus $\ln(t)$ shown in Figure 4.2 exhibits a sharp break in the curve for values of $\ln t$ larger than one. This is interpreted to mean that there is a change in the mode of crystallization at this point. These results are consistent with a change from a primary crystallization process to a secondary crystallization process. It is not clear precisely what is happening in each of the two stages of crystallization, but a reasonable hypothesis is that crystals are nucleated and rapidly grown to some small, finite size during the primary crystallization stage. During the secondary crystallization the crystals may increase in size and perfection.

In this research the value of the Avrami exponent for the primary crystallization, n was found to vary from 1.75 for a SDR of 210 to 1.34 for a SDR of 660.

According to classical theory, the values of n near two suggest either plate-like growth from pre-existing nuclei or fibrillar growth with constant heterogeneous nucleation rate. Values of n near unity suggest fibrillar growth from pre-existing nuclei (See Table III). If this theory is correct, our values of n suggest that there is a plate-like and/or fibrillar growth from pre-existing nuclei.

As discussed earlier, k is a kinetic constant which includes the rate for both nucleation and growth. Direct measurement of the nucleation rates were not possible, but the constant k provides important information about this process. If it is assumed that growth rates are affected by orientation, variation in the value of k for different SDR's may be explained through the nucleation mechanism and degree of initial orientation of the sample.

In this research, the value of k varied from 8×10^{-4} to 120×10^{-4} for a SDR of 210 to 660 respectively. The change in the value of k through a factor of fifteen can be attributed to higher nucleation rates for samples with higher initial orientation due to the higher SDR's.

TABLE III
MECHANISM OF CRYSTALLIZATION AND THE VALUE OF n

Growth	Homogeneous nucleation	Heterogeneous nucleation
Three-dimensional	4	$3 \leq n \leq 4$
Two-dimensional	3	$2 \leq n \leq 3$
One-dimensional	2	$1 \leq n \leq 2$

The Structure of As-Spun and Conditioned Filaments

Results. Figure 4.4 shows the WAXS patterns for as-spun filaments spun on the MPE at different SDR's. All samples show a single broad peak on the equator. At higher SDR's an intense meridional reflection exists at a lower diffraction angle. A typical diffractometer scan along the equator and along the meridian is shown in Figure 4.5 for a sample with SDR = 240. The meridional reflection occurs at $2\theta = 11^\circ$ while the equatorial peak occurs at $2\theta = 22^\circ$. Figure 4.6 shows the effect of SDR on the 0, 14, 0 peak. The peak shifts from $2\theta = 78.5^\circ$ to 79.4° as the SDR changes from 15 to 240. Figure 4.7 shows the effect of SDR on the relative amounts of phases present in the filament. The total crystallinity goes up slightly with SDR. The γ crystalline fraction goes up with SDR and α crystalline fraction is reduced correspondingly. These results were calculated by a new procedure as described in Chapter III. The results are also shown in Table IV where corresponding density data and crystalline chain axis orientation functions for each sample are also given. The chain axis crystalline orientation factor is plotted in Figure 4.8 as a function of SDR for both Instron and MPE samples.

Discussion. The spun and conditioned fibers exhibit very broad diffraction peaks. The peaks are sufficiently well-defined to indicate that the samples are no longer entirely amorphous but are partially crystalline. Presumably the crystals have formed during conditioning by the cold crystallization process described previously. The crystals that have formed must be very small and/or paracrystalline in order to account for the breadth of the diffraction peaks. The diffractometer

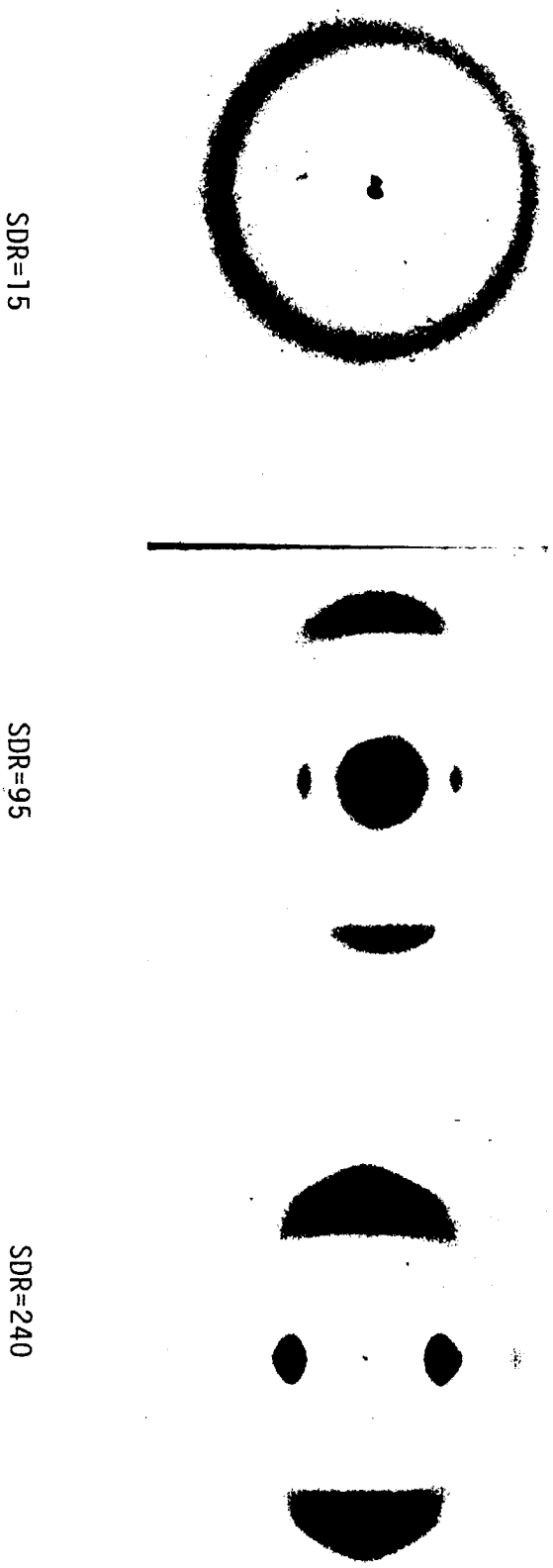


Figure 4.4. MAXS Patterns of Spun and Conditioned Nylon-6 Filaments

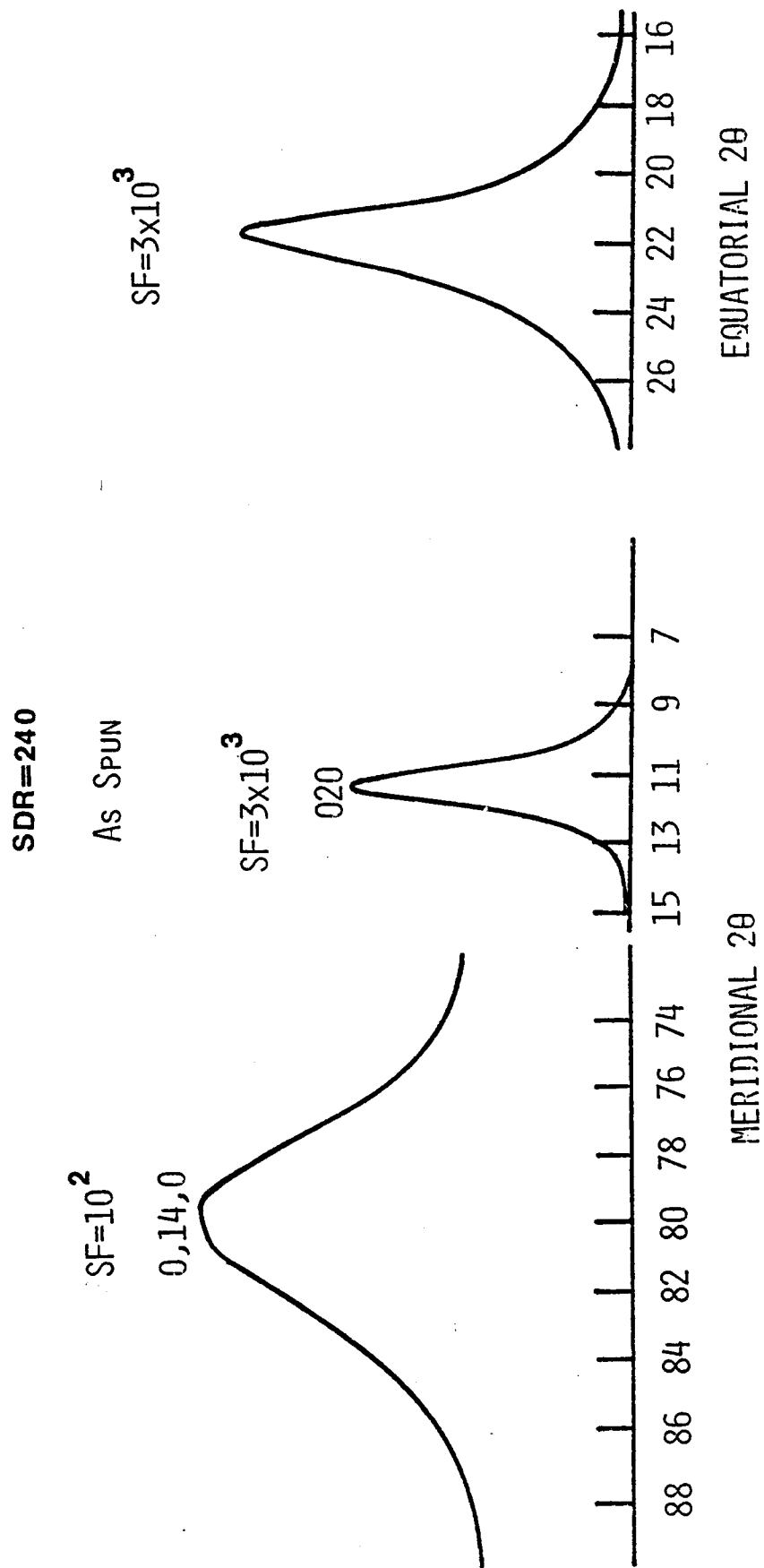


Figure 4.5. WAXS Patterns for As-Spun and Conditioned Nylon-6.

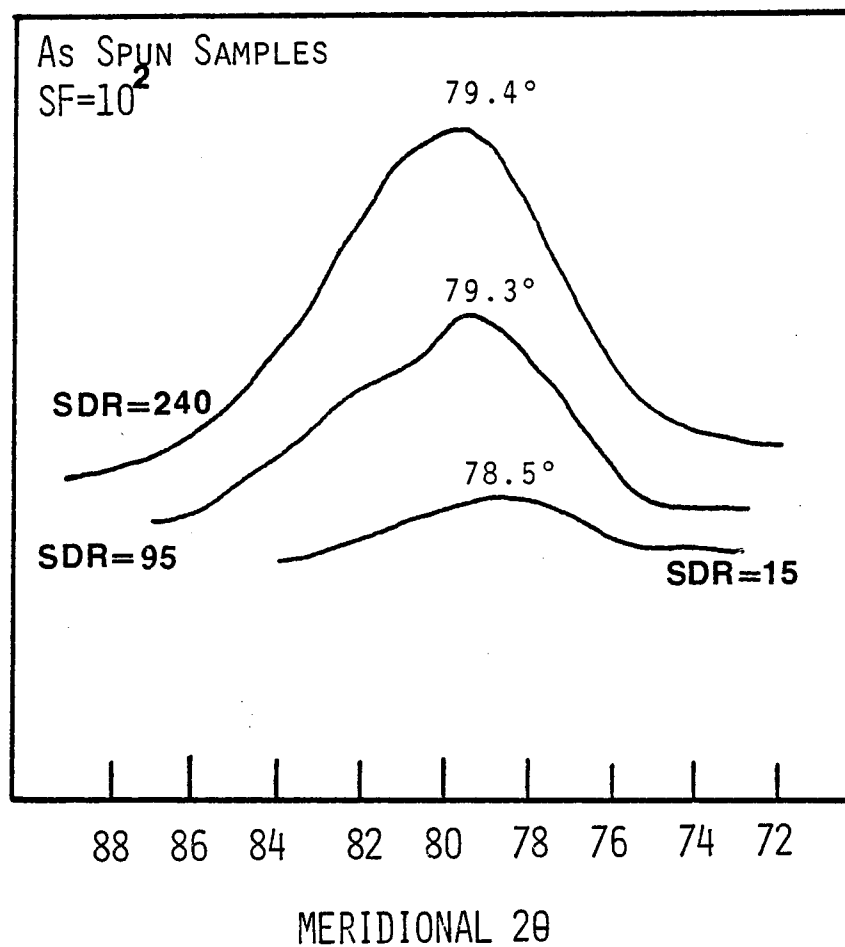


Figure 4.6. The Effect of SDR on the 0,14,0 Peak.

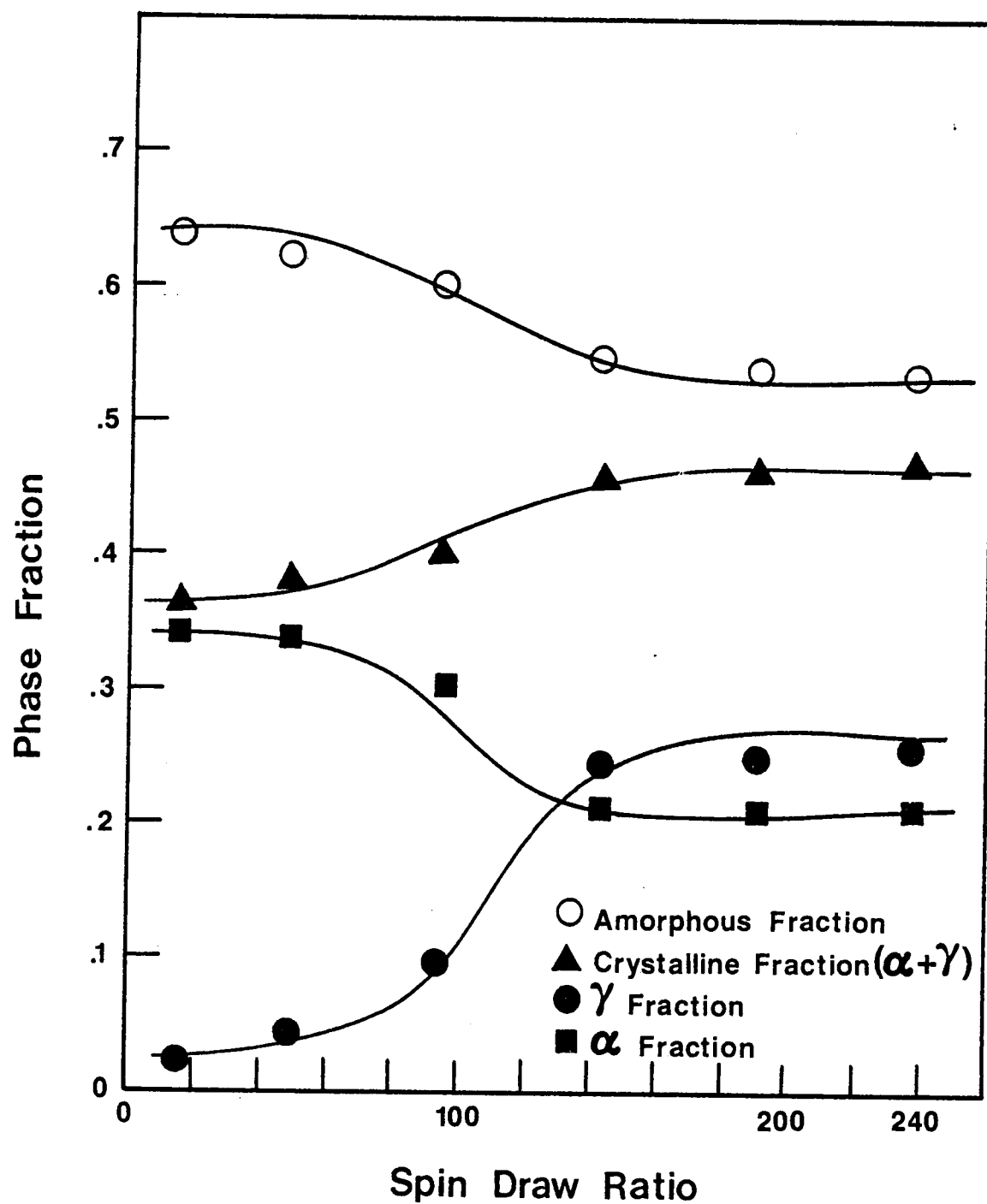


Figure 4.7. Phase Fractions of Nylon-6 as a Function of SDR.

TABLE IV
 VARIOUS PHASE FRACTIONS OF AS-SPUN AND CONDITIONED FILAMENTS OF NYLON-6

Spin Draw Ratio SDR	γ Fraction	α Fraction	Crystalline Fraction	Amorphous Fraction	Density	Chain Axis Orientation
15	.022	.341	.363	.637	1.1288	.07
48	.043	.337	.380	.620	1.1301	.20
95	.093	.307	.400	.600	1.1303	.50
142	.245	.211	.456	.544	1.1303	.66
190	.251	.212	.463	.537	1.1310	.69
240	.254	.213	.467	.533	1.1315	.71

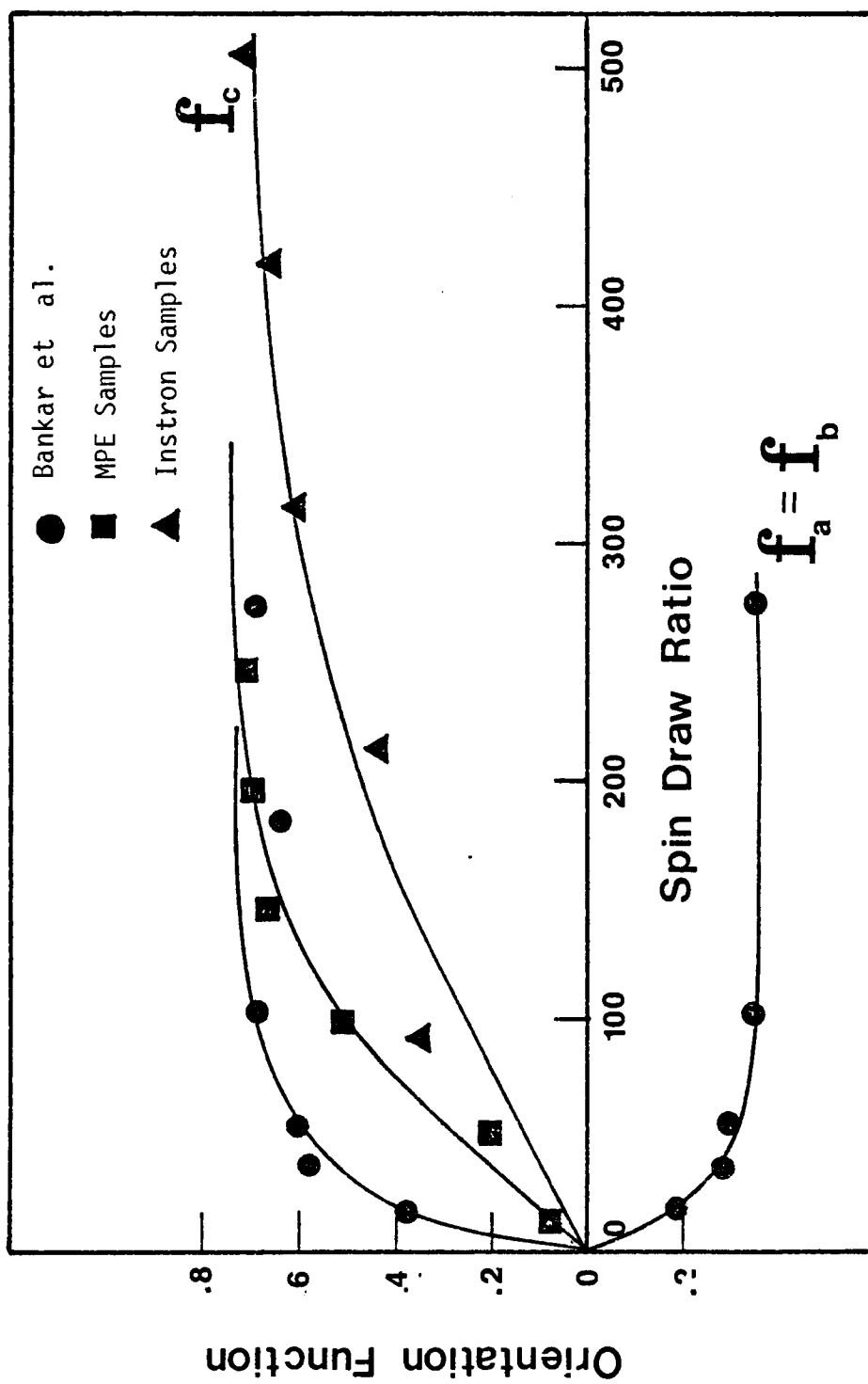


Figure 4.8. Orientation Function of Spun and Conditioned Nylon-6 Fibers as a Function of SDR.

scans indicate that in this rather imperfect form the crystals exhibit pseudohexagonal symmetry.

Parker and Lindenmeyer (73) have measured the 0, 14, 0 reflections in nylon-6 fibers. According to their measurement of the 0, 14, 0 reflection in oriented fibers will distinguish between the two crystalline phases, (i.e. α and γ phases) which are commonly observed in nylon-6 fibers. Their argument is based on the fact that the 0, 14, 0 reflection occurs at $2\theta = 78^\circ$ for the γ -phase but at 80° for the α -phase. Figure 4.6 shows the effect of SDR on 0, 14, 0 peak. At low SDR's the peak occurs at about 78.5° and shifts to higher angle with increasing SDR. This trend would seem to result from an increased tendency for γ -phase formation. Qualitatively similar interpretation is arrived at by examining the increase in relative intensity of the 020 meridional reflection. A γ index method was used to characterize that trend more quantitatively. Calculation for the different phase fraction was done as described in Chapter III. Figure 4.7 shows the effect of SDR on the various crystalline and amorphous phases. It is observed that the filaments spun at very low SDR have a low γ phase content ($X_\gamma < 0.1$) but a high paracrystalline α phase content ($X_\alpha = 0.35$). As SDR increases the α phase content decreases while the γ phase content and total crystalline content increase. At high SDR's, the phase content levels out at about $X_\gamma = 0.25$ while the α phase content levels at about $X_\alpha = 0.2$. It may be noted that the observation of pseudohexagonal symmetry does not necessarily imply the presence of γ phase nor the absence of paracrystalline α phase.

Both the data for the 0, 14, 0 reflection and the relative intensity of the meridional peak may be interpreted to indicate that a very

imperfect paracrystalline α phase predominates at low SDR's and this is the interpretation used here.

The chain axis crystalline orientation function increases with increasing SDR for both the MPE and Instron samples, Figure 4.8. However, this increase is more gradual for the Instron samples. This may be due to the faster spinning speeds used in spinning of the MPE samples, and the resultant higher cooling rate along the threadline. This in turn may result in higher spinline stresses for the MPE samples at similar SDR's. Prior work of Nadella et al. (72) shows that orientation and morphology of spun filaments of polypropylene correlates with spinline stress independent of secondary variables such as take-up velocity, extrusion rate, etc. This could explain the differences shown in Figure 4.8 but cannot be checked because the spinline stresses were not measured in the present study.

The Annealing of Conditioned Filaments

Results of Annealing. Figure 4.9 shows the changes in birefringence due to annealing of the MPE samples in boiling water and formic acid. Figure 4.10 shows the effect on birefringence of annealing in room temperature water and boiling water (Instron samples). In all cases, the birefringence changes as a function of the annealing medium and the temperature of that medium. Figures 4.11 and 4.12 show the changes in density due to annealing in water and formic acid. The effects of annealing of as-spun MPE fibers in water and formic acid are shown in WAXS patterns of Figure 4.13. The meridional peak corresponding to a d-spacing of $8.2 \text{ \AA}$ ($2\theta = 11^\circ$) slowly disappears and the equatorial peak of $4.13 \text{ \AA}$ ($2\theta = 22^\circ$) splits into two reflections. The formic

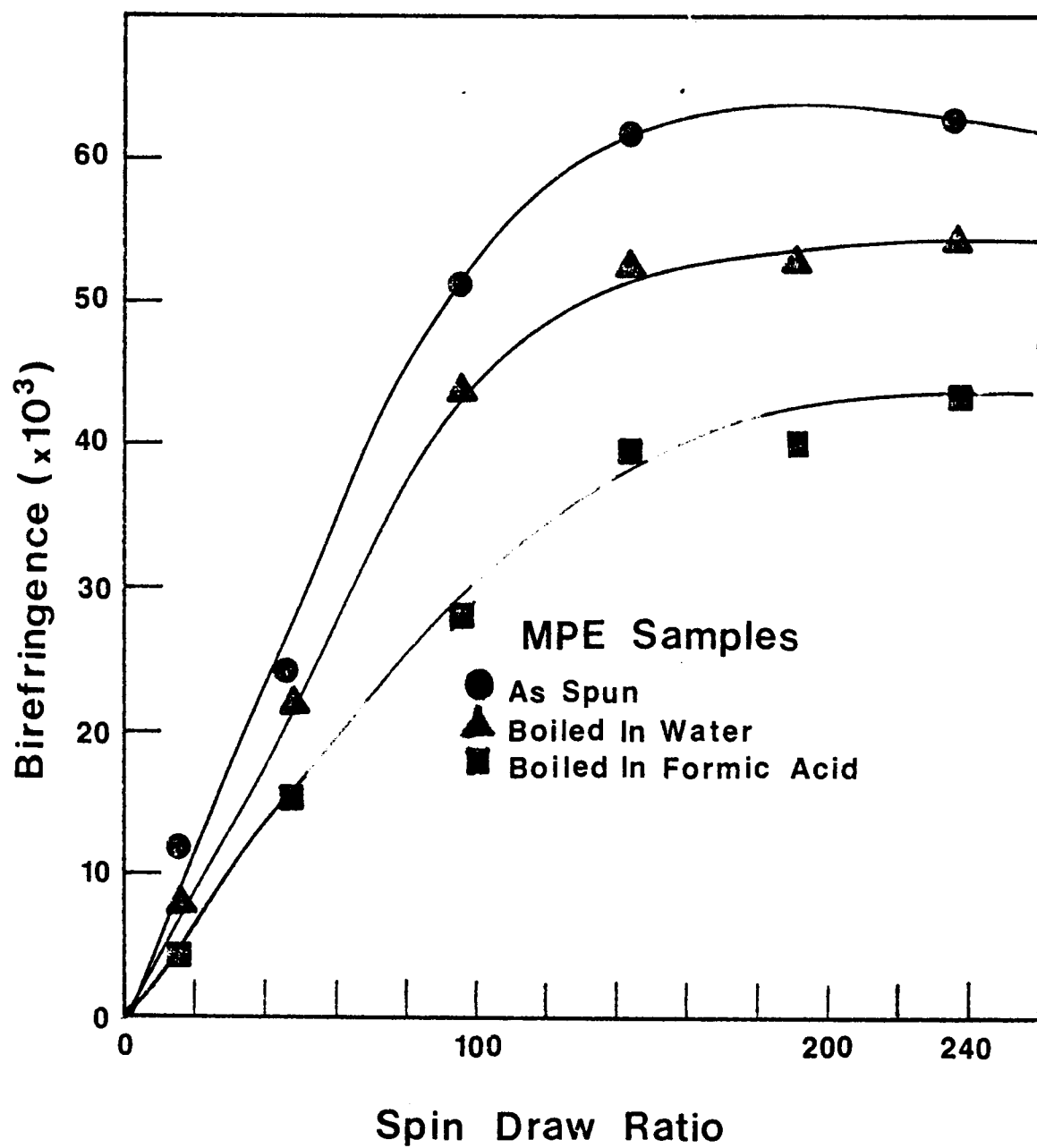


Figure 4.9. Birefringence of As-Spun and Annealed Samples as a Function of SDR.

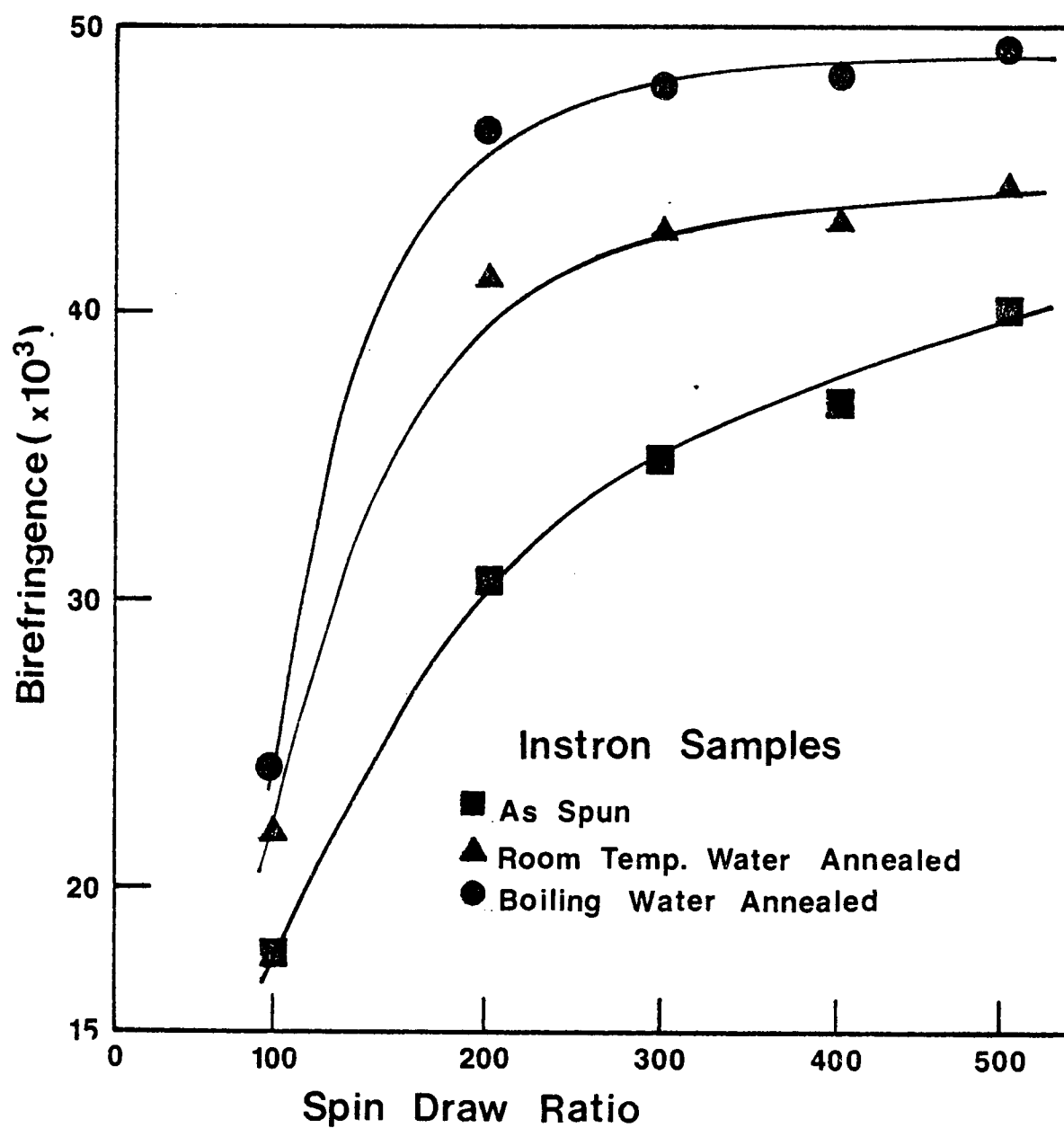


Figure 4.10. Birefringence of As-Spun and Annealed Samples as a Function of SDR.

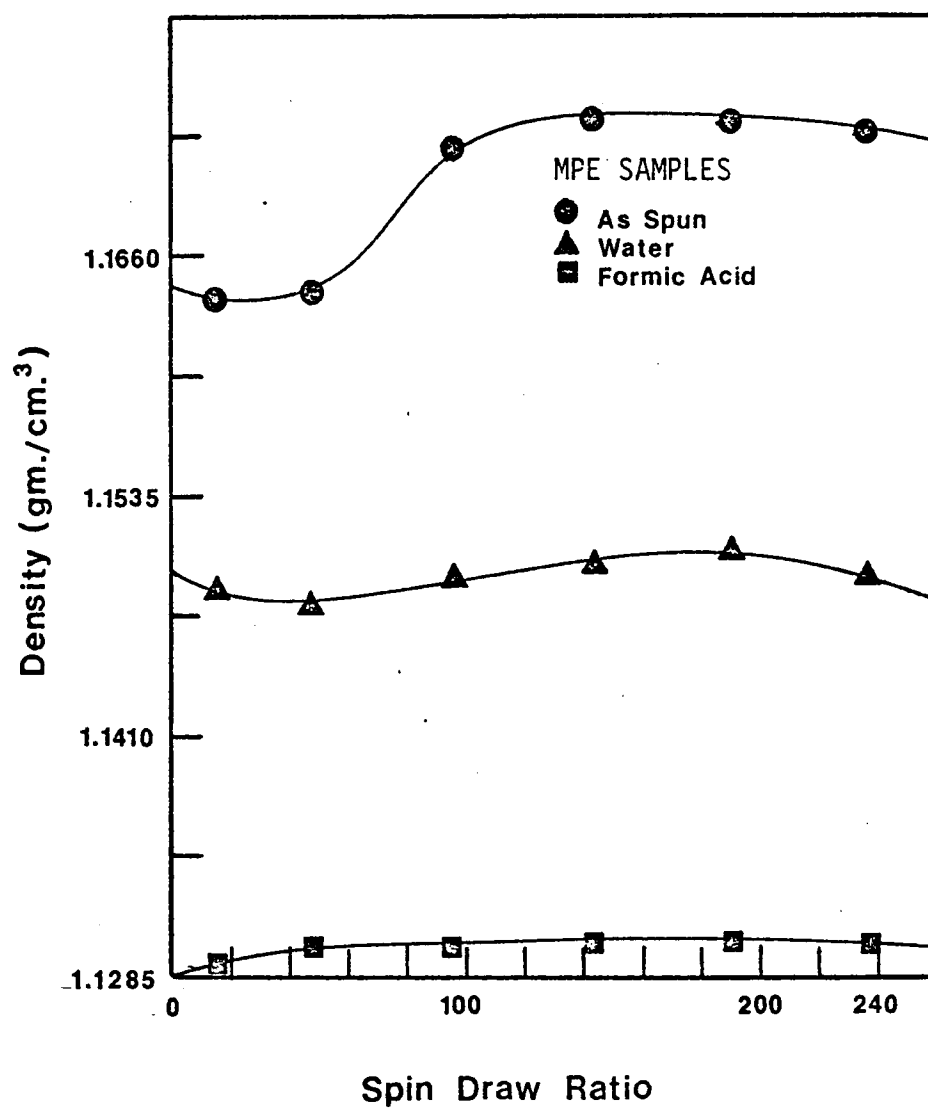


Figure 4.11. Densities of As-Spun and Annealed Samples as a Function of SDR.

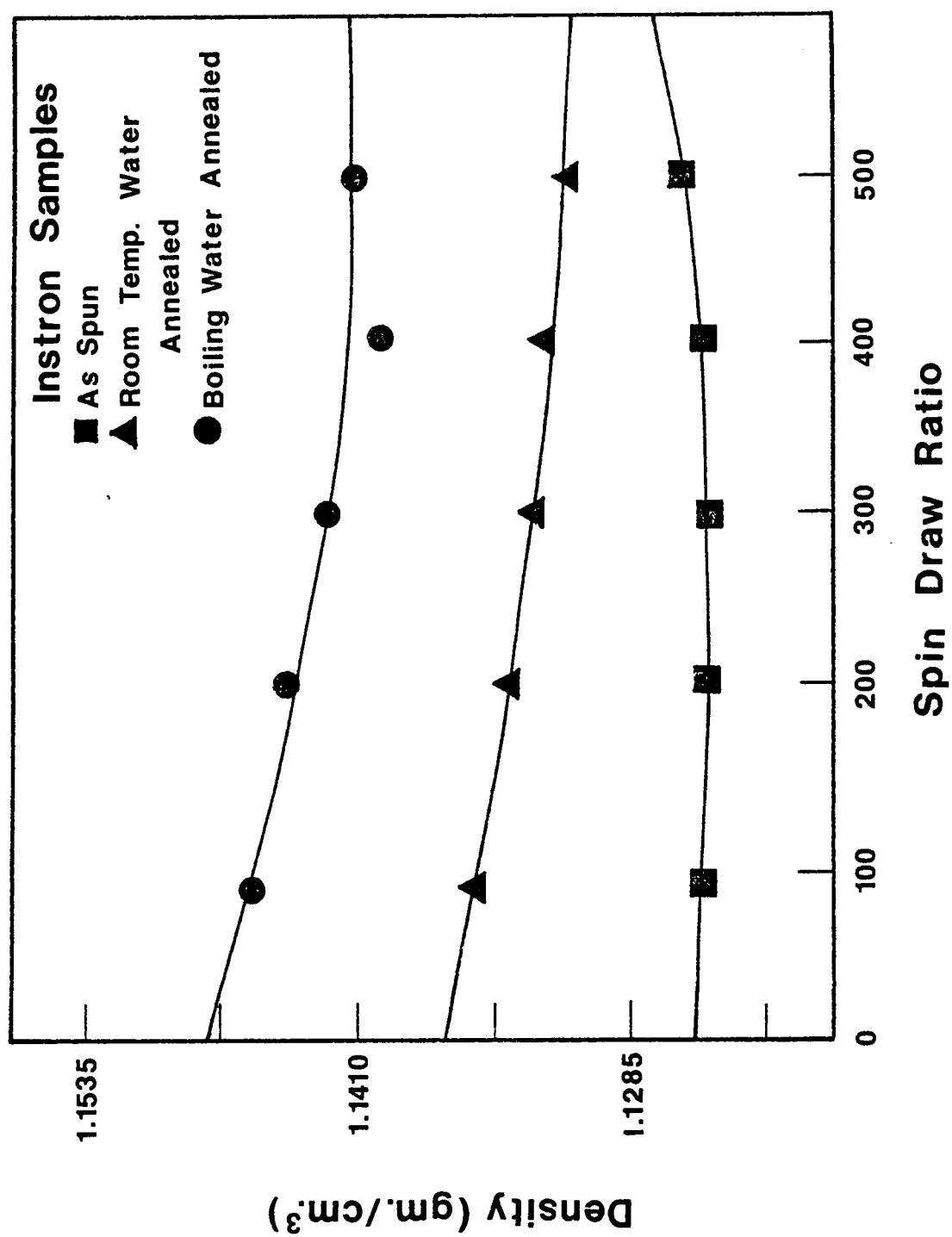
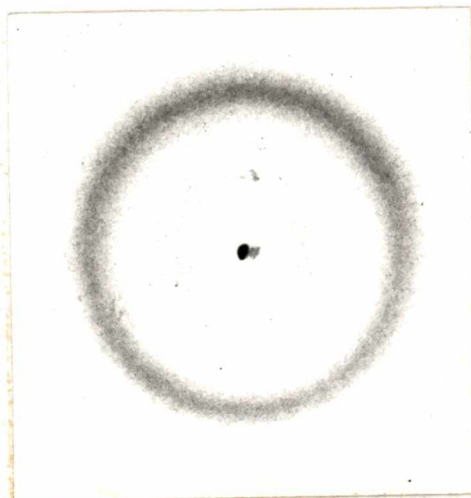


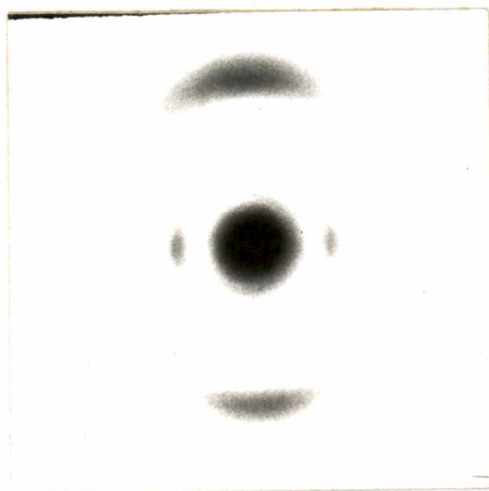
Figure 4.12. Densities of As-Spun and Annealed Samples as a Function of SDR.

SDR = 48



SDR = 95

AS - SPUN



SDR = 240

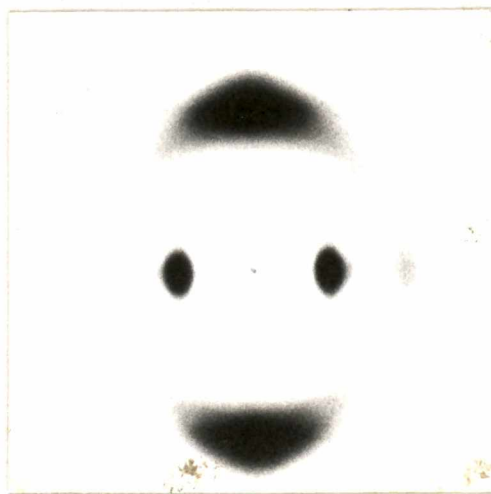


Figure 4.13. Effect of Annealing on the WAXS Patterns of Nylon-6.

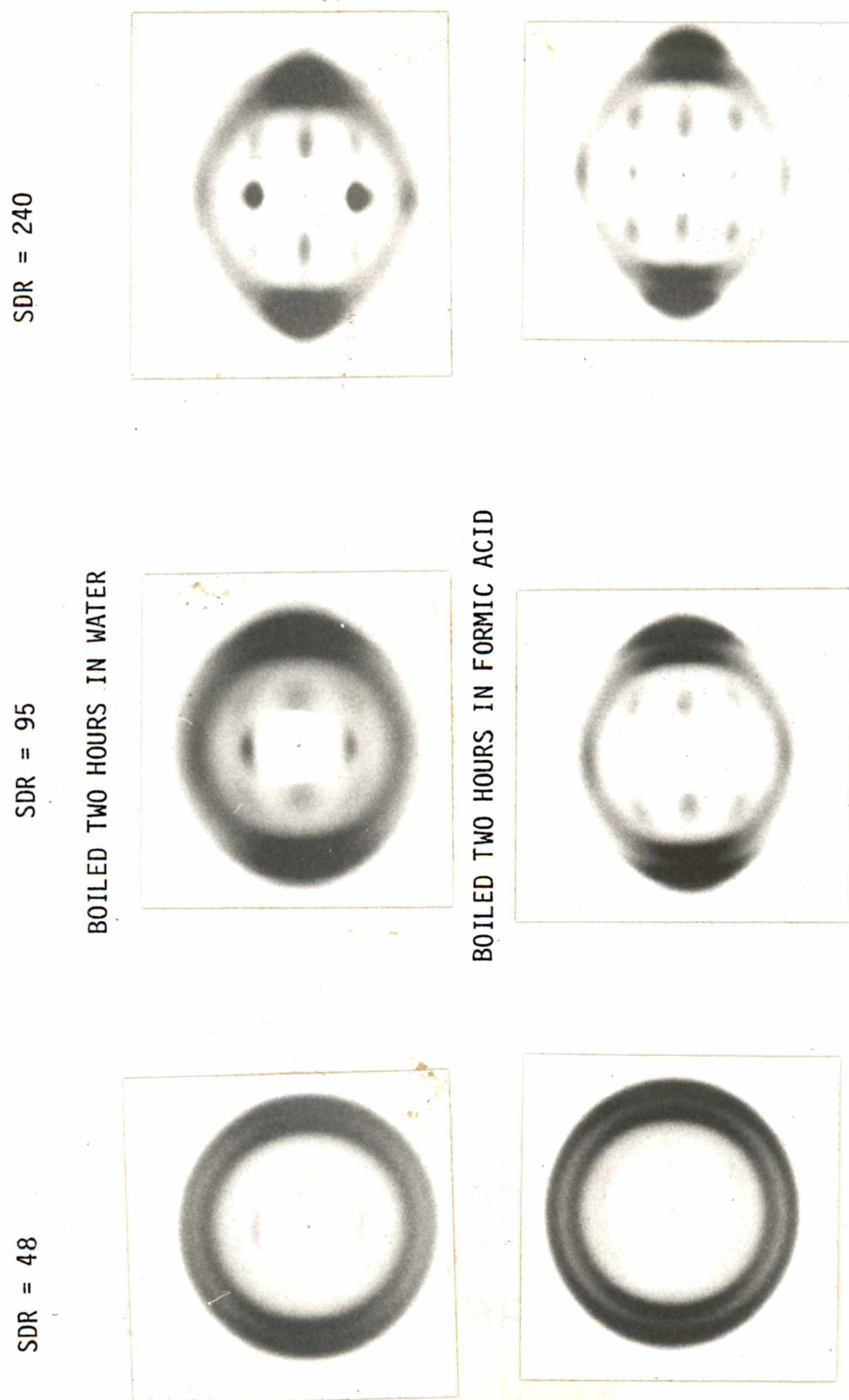


Figure 4.13. (Continued) Effect of Annealing on the WAXS Patterns of Nylon-6.

acid seems to be more effective as an annealing medium than either water or partial vacuum.

Figures 4.14 through 4.25 show the effect of different annealing treatments on the WAXS diffractometer scans of nylon-6.

Figures 4.26 and 4.27 show the analysis of the WAXS data by use of the γ index. Figure 4.26 shows the γ phase decreases on annealing in water or formic acid. Figure 4.28 shows how the total crystalline fraction is increased by annealing in water or formic acid. Table V shows the crystallinity indices calculated and corresponding density and chain axis orientation data.

Figure 4.29 shows the changes in chain axis crystalline orientation as determined from wide angle X-ray diffraction.

Discussion. The general trend is that the fibers initially showing a pseudohexagonal structure develop into a monoclinic structure due to annealing. Figure 4.14 through 4.25 show the effects of annealing in water, formic acid and partial vacuum on the WAXS patterns of nylon-6. The formation of the α -monoclinic phase causes the splitting of the equatorial reflections, diminishing of the 020 reflection and a shift in the position of the 0, 14, 0 reflection. Annealing in formic acid thus results in the formation of an α -monoclinic phase. There is evidence that the water annealed sample is a mixture of α and γ phases.

In partial vacuum, annealing at temperatures below 140°C results in very little conversion to the α -monoclinic structure. At annealing temperatures above 140°C a shift toward the α -monoclinic phase is observed. It should be noted that annealing at higher temperatures (140°C) causes both a change in the type of crystals and an increase in

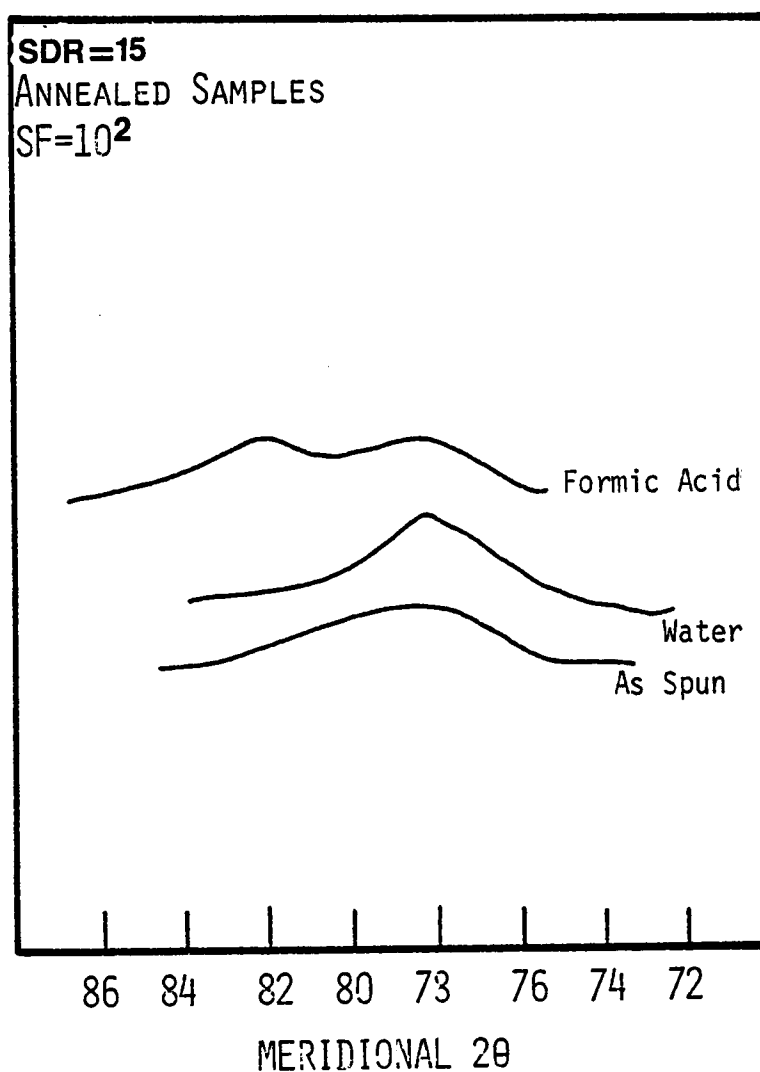


Figure 4.14. Effect of Annealing on the 0,14,0 Peak (SDR 15).

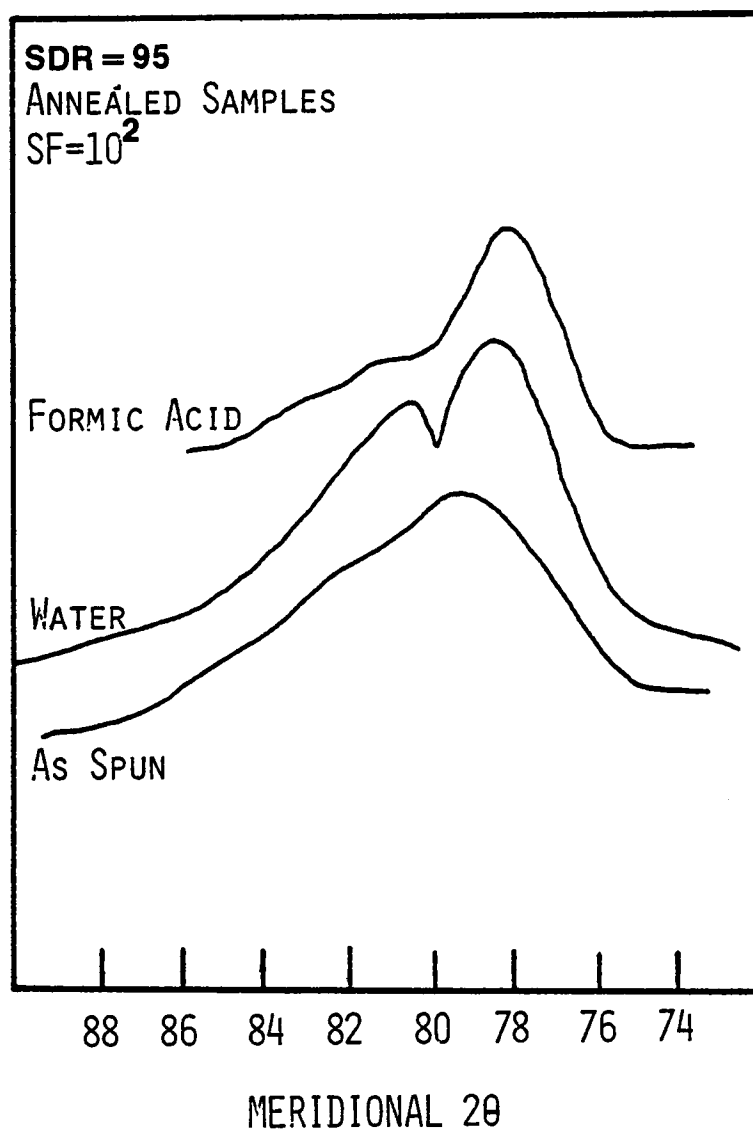


Figure 4.15. Effect of Annealing on 0,14,0 Peak (SDR 95).

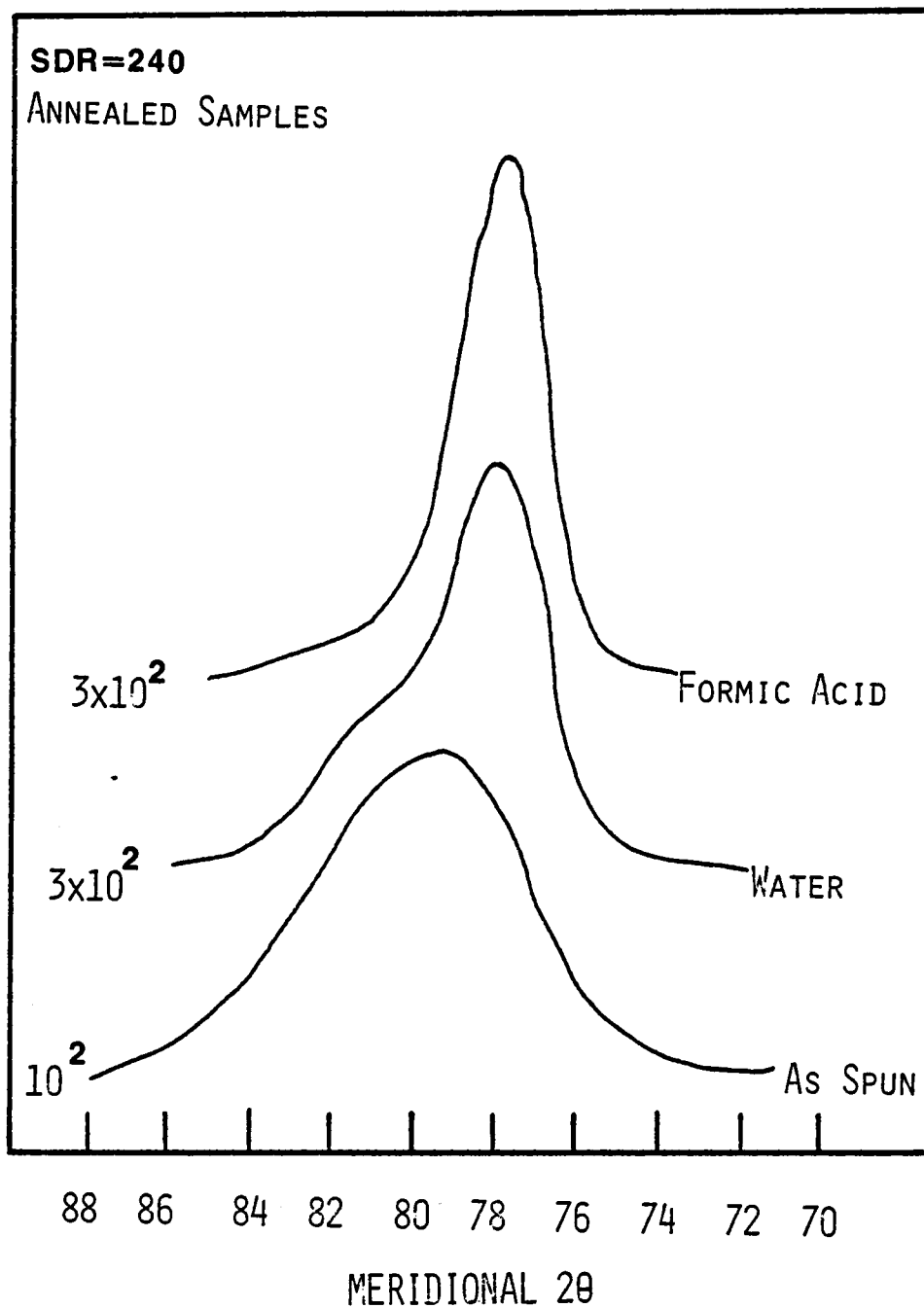


Figure 4.16. Effect of Annealing on 0,14,0 Peak (SDR 240).

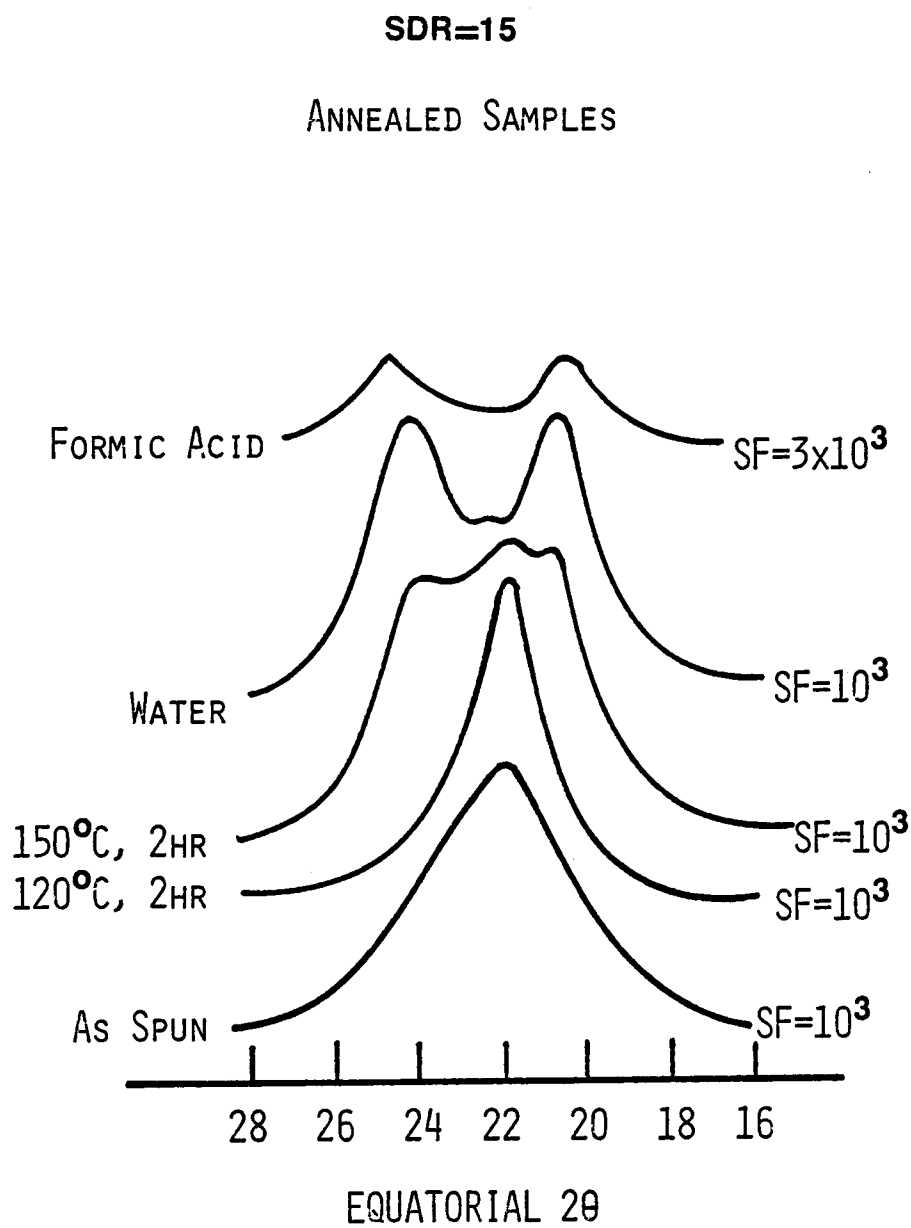


Figure 4.17. Effect of Annealing in Formic Acid Water and Partial Vacuum (SDR 15).

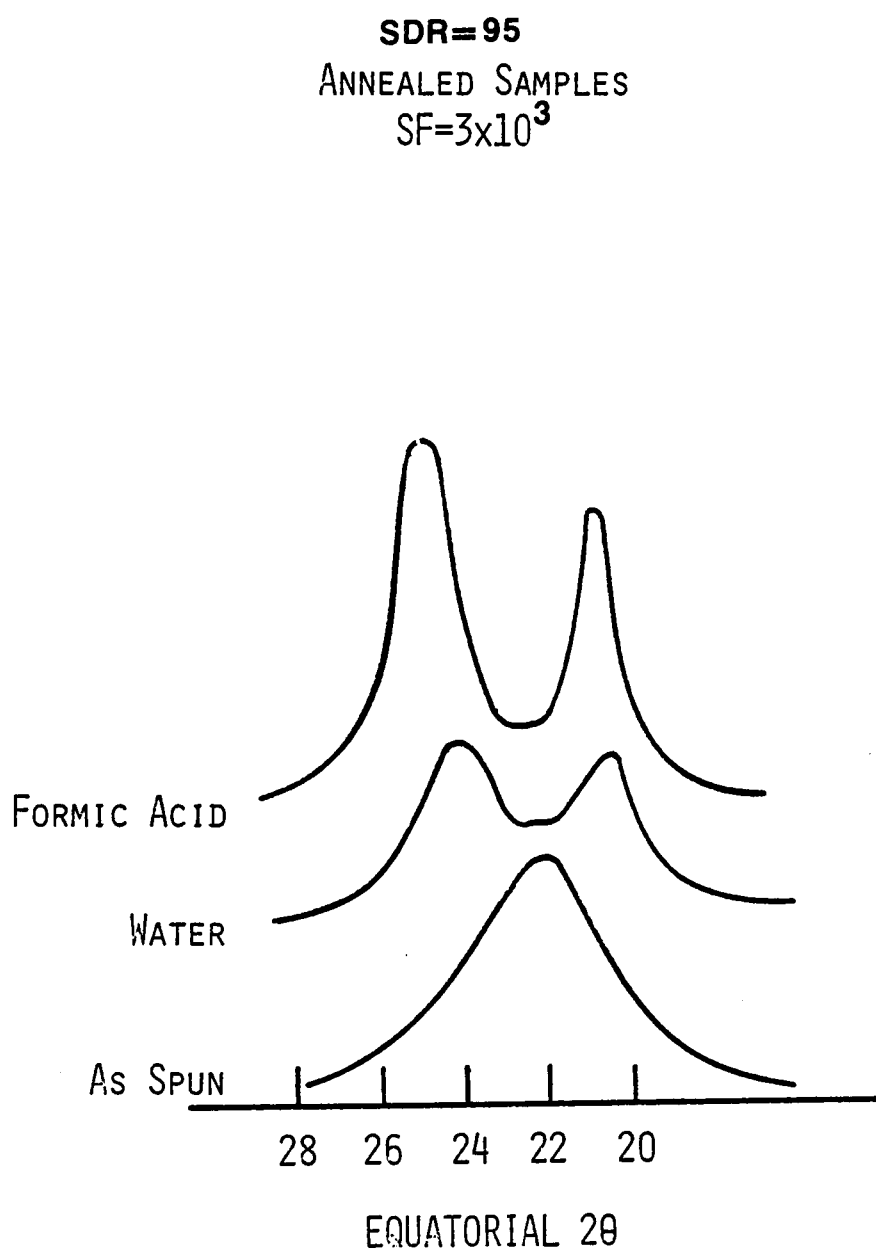


Figure 4.18. Effect of Annealing in Formic Acid and Water (SDR 95).

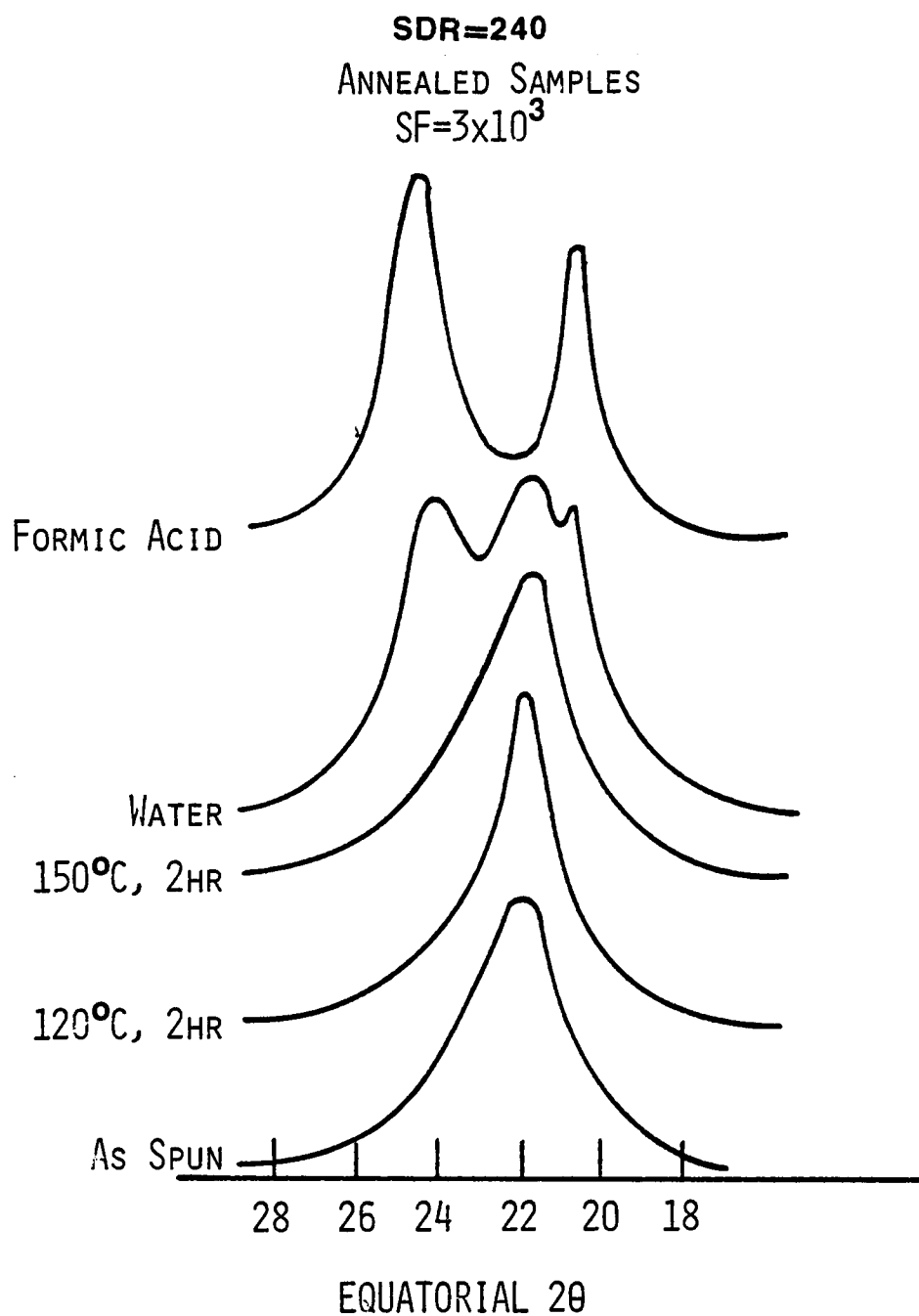


Figure 4.19. Effect of Annealing in Formic Acid, Water and Partial Vacuum (SDR 240).

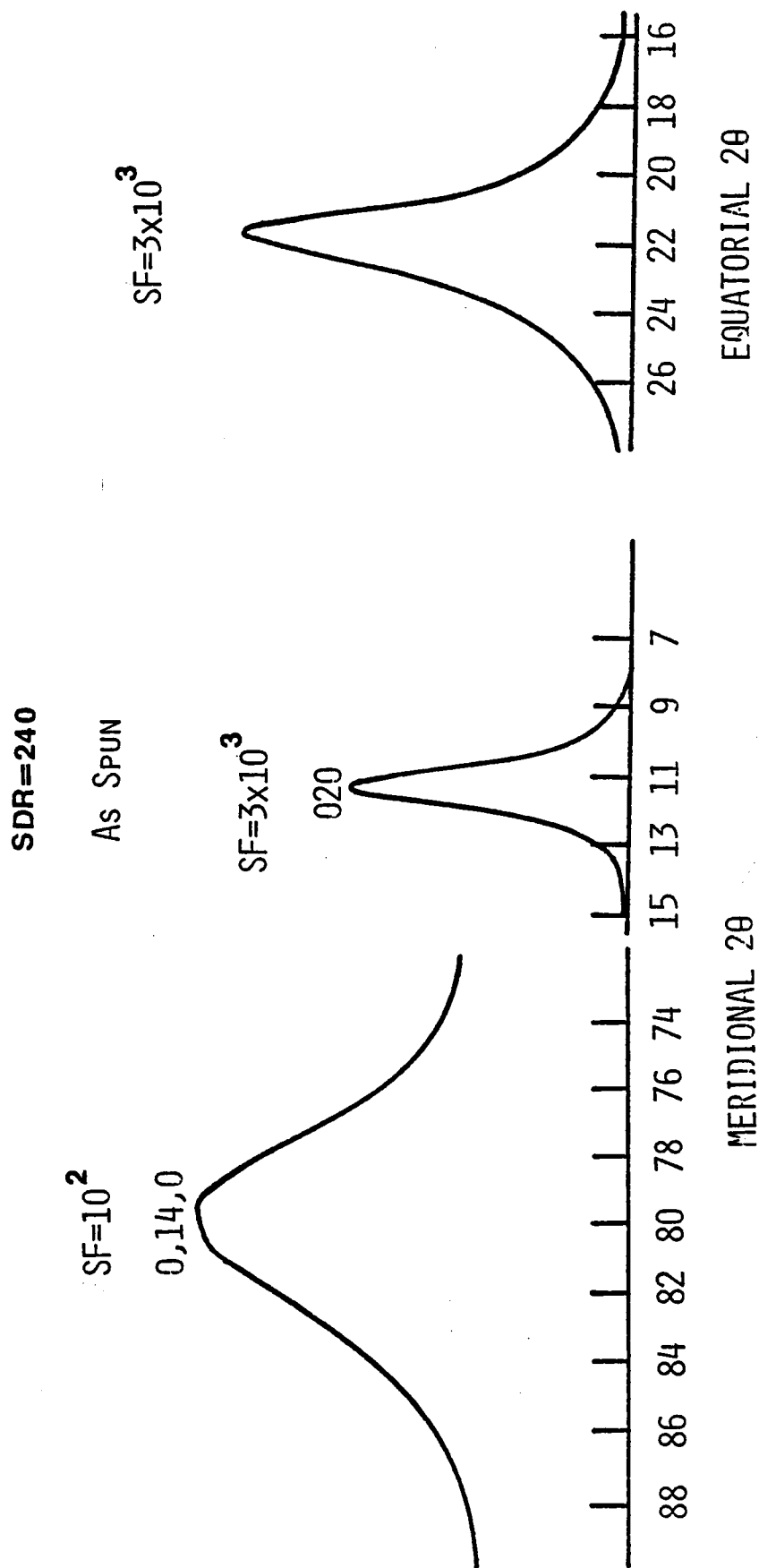


Figure 4.20. WAXS Patterns for As-Spun and Conditioned Fiber (SDR 240).

SDR=240

ANNEALED, 120°C, 2HR

$SF=3 \times 10^3$

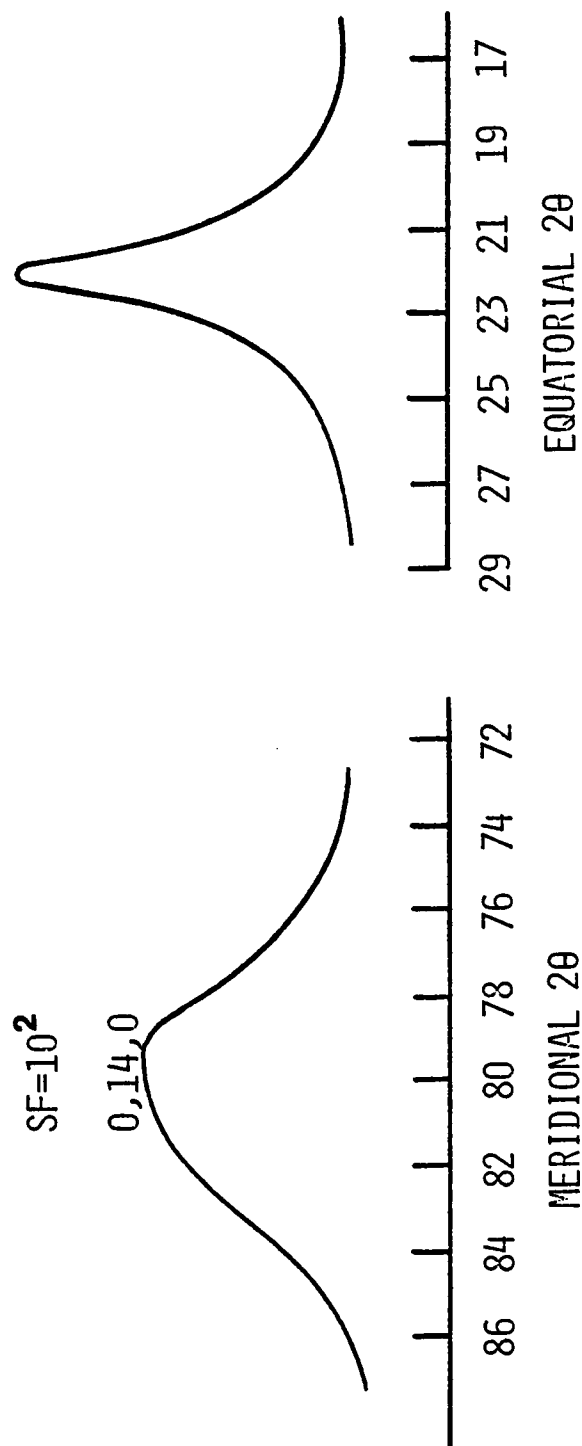


Figure 4.21. WAXS Patterns for As-Spun and Conditioned Fibers Annealed in Partial Vacuum at 120°C, 2 Hours (SDR 240).

SDR=240

ANNEALED 2HR, 140°C, VACUUM

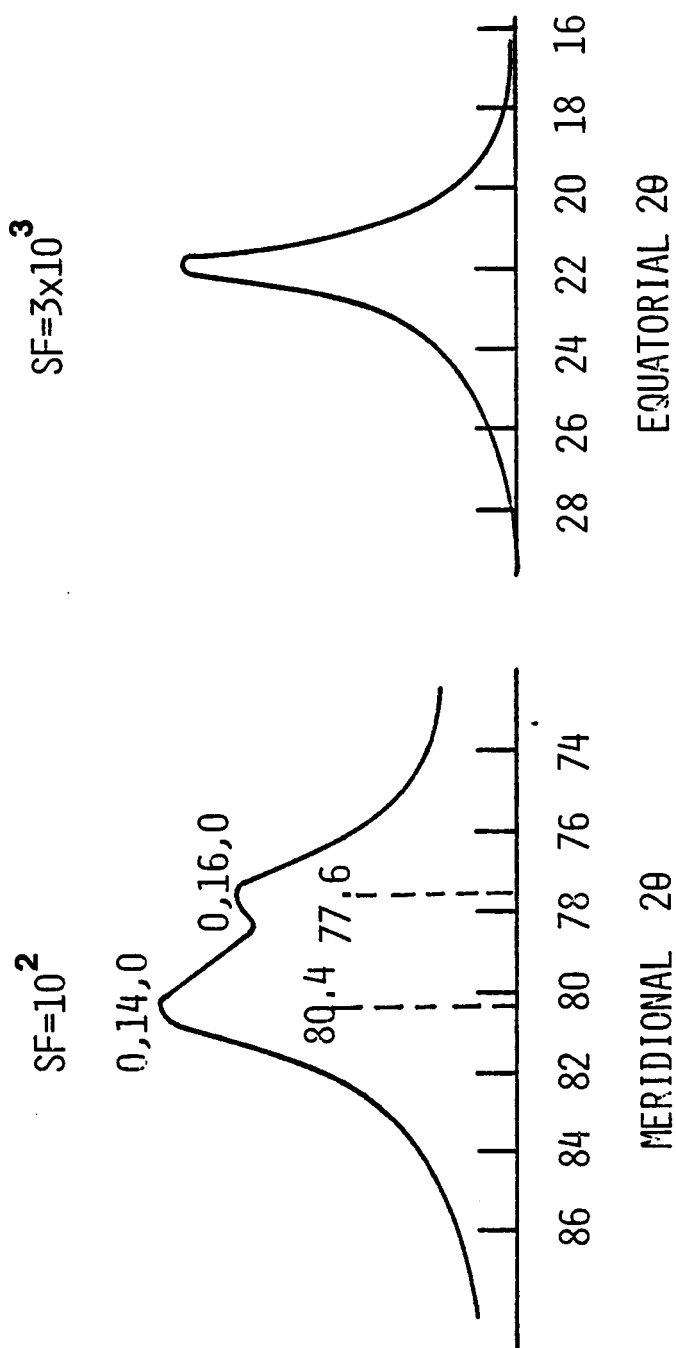


Figure 4.22. WAXS Patterns for As-Spun and Conditioned Fibers Annealed in Partial Vacuum at 140°C, 2 Hours (SDR 240).

SDR=240

ANNEALED 2HR, 150°C, VACUUM

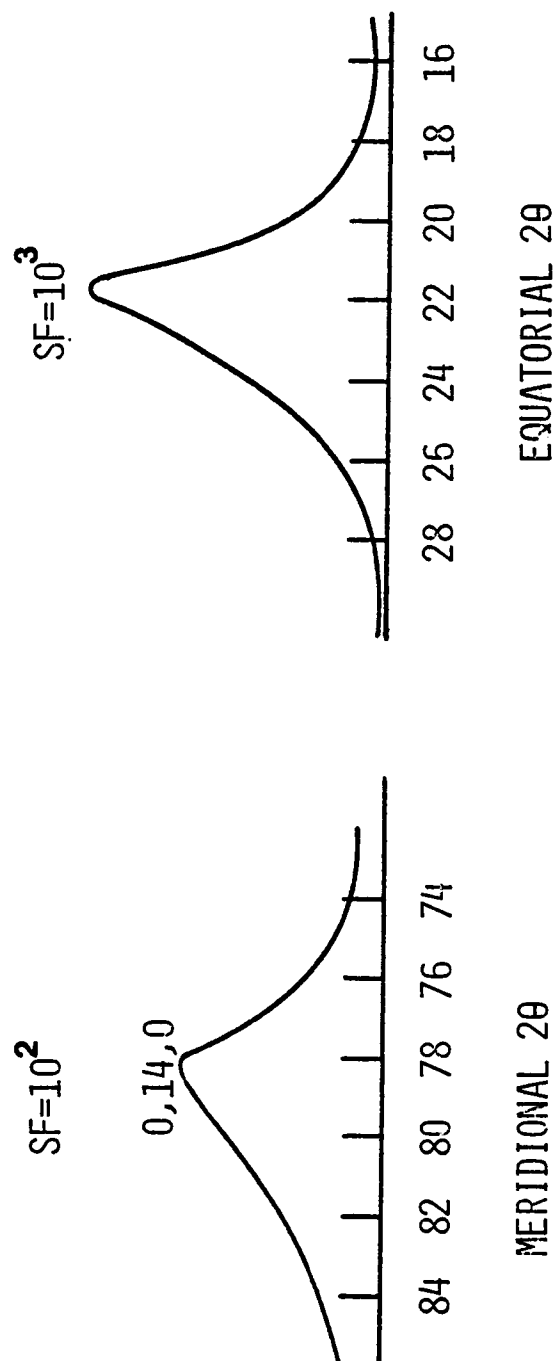


Figure 4.23. Waxes Patterns for As-Spun and Conditioned Fibers Annealed in Partial Vacuum at 150°C, 2 Hours (SDR 240).

SDR=240

BOILED IN WATER, 2HR

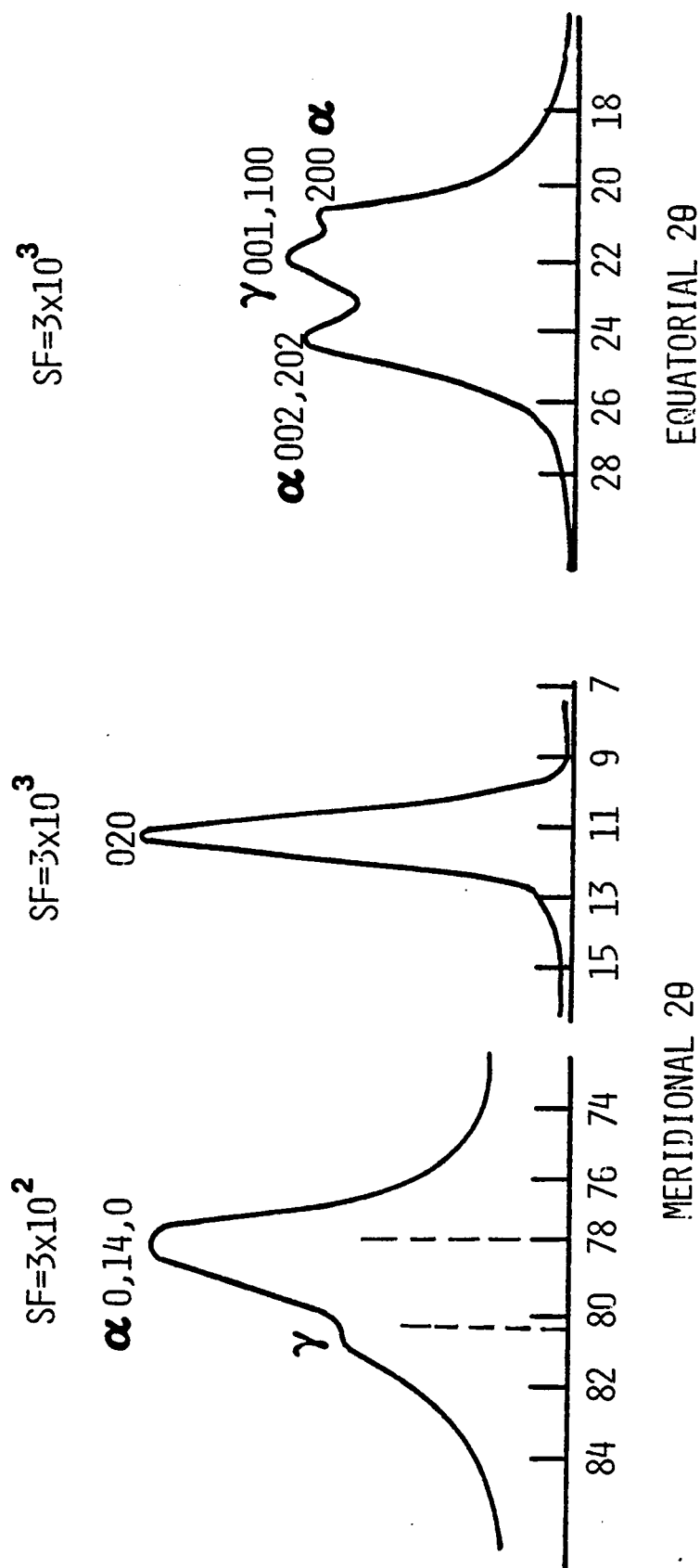


Figure 4.24. WAXS Patterns for As-Spun and Conditioned Fibers Annealed in Boiling Water for 2 Hours (SDR 240).

SDR=240

20% FORMIC ACID, 2HR

$SF=3 \times 10^2$

0,14,0

$SF=3 \times 10^2$

020

$SF=3 \times 10^3$

α 002,202

α 200

MERIDIONAL 2θ

EQUATORIAL 2θ

Figure 4.25. WAXS Patterns for As-Spun and Conditioned Fibers Annealed in Boiling Formic Acid Solution for 2 Hours (SDR 240).

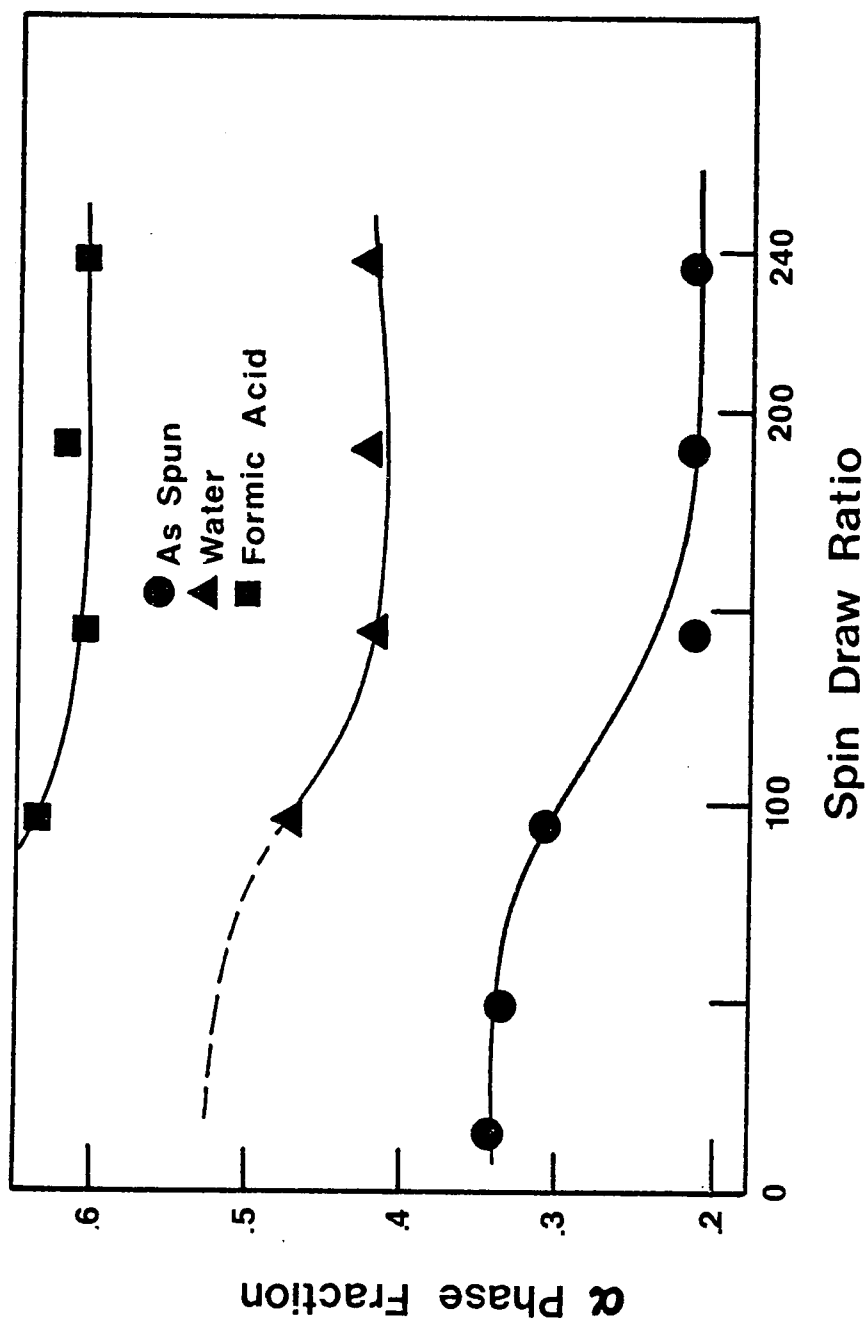


Figure 4.26. α Phase Fraction of As-Spun and Annealed Samples as a Function of SDR.

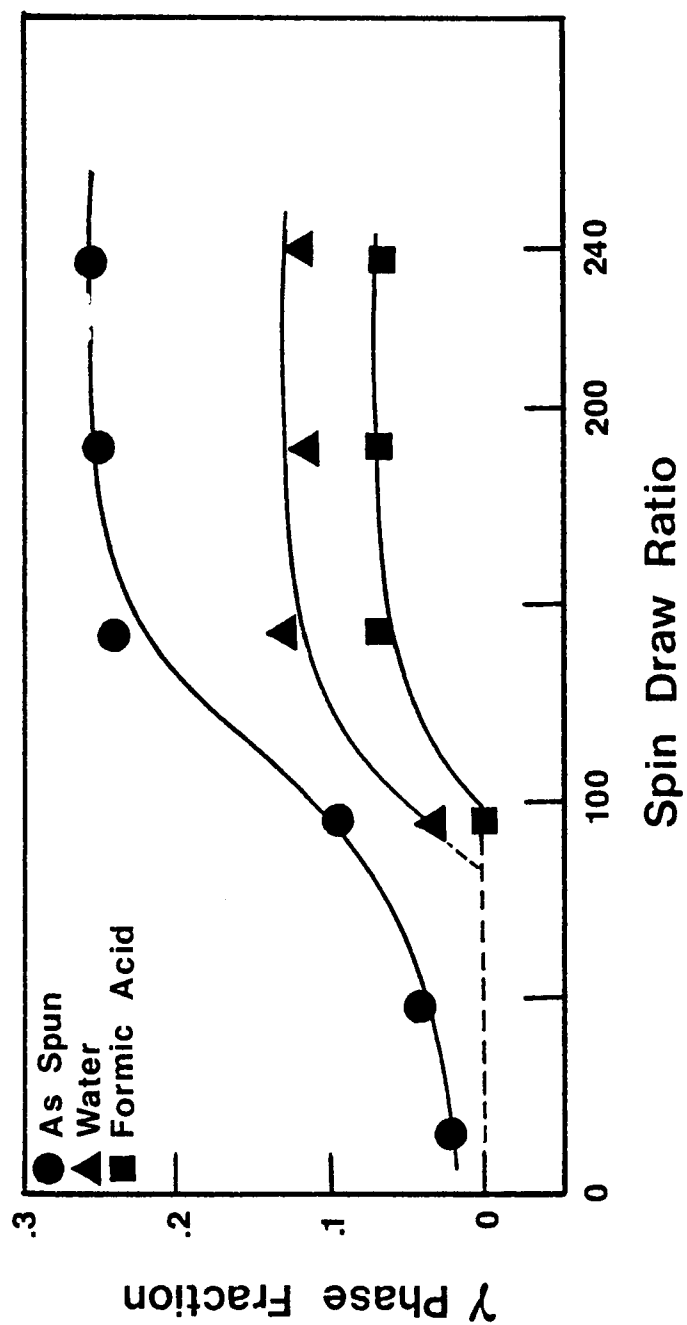


Figure 4.27. γ Phase Fraction of As-Spun and Annealed Samples as a Function of SDR.

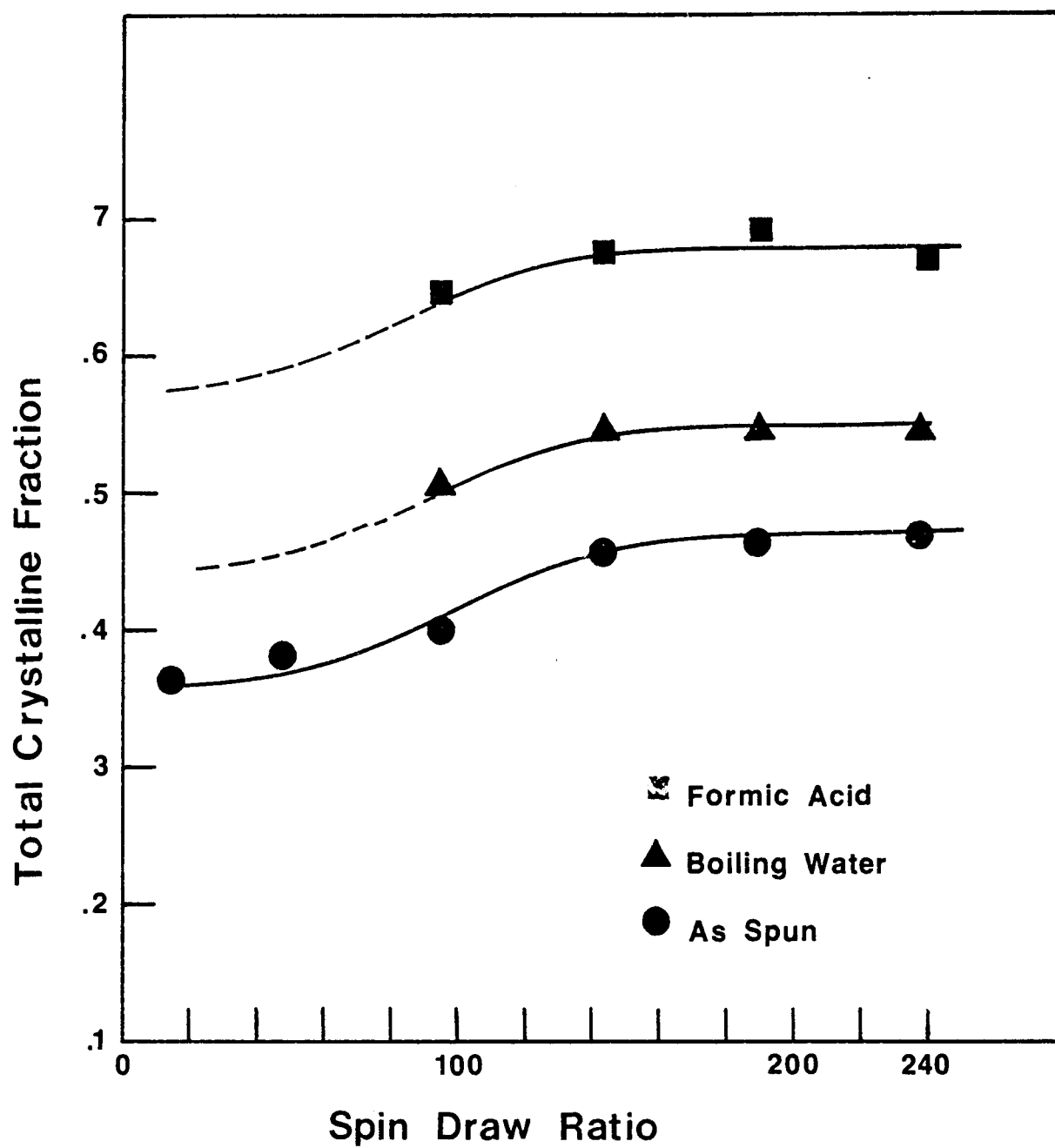


Figure 4.28. Total Crystalline Fraction of As-Spun and Annealed Samples as a Function of SDR.

TABLE V
VARIOUS PHASE FRACTIONS OF AS-SPUN AND ANNEALED FILAMENTS OF NYLON-6

Spin Draw Ratio	γ Fraction	α Fraction	Total Crystalline Fraction	Amorphous Fraction	Density	Chain Axis Orientation
95	.093	.307	.400	.600	1.1303	.50
Water	.032	.473	.505	.495	1.1491	.62
Formic Acid	.009	.635	.645	.355	1.1716	.68
142	.245	.211	.456	.544	1.1303	.66
Water	.126	.418	.545	.455	1.1498	.72
Formic Acid	.069	.606	.675	.325	1.1729	.75
190	.251	.212	.463	.537	1.1310	.69
Water	.111	.432	.543	.457	1.1504	.74
Formic Acid	.067	.626	.693	.307	1.1729	.73
240	.254	.213	.467	.533	1.1315	.71
Water	.115	.422	.537	.463	1.1493	.75
Formic Acid	.065	.605	.670	.330	1.1723	.73

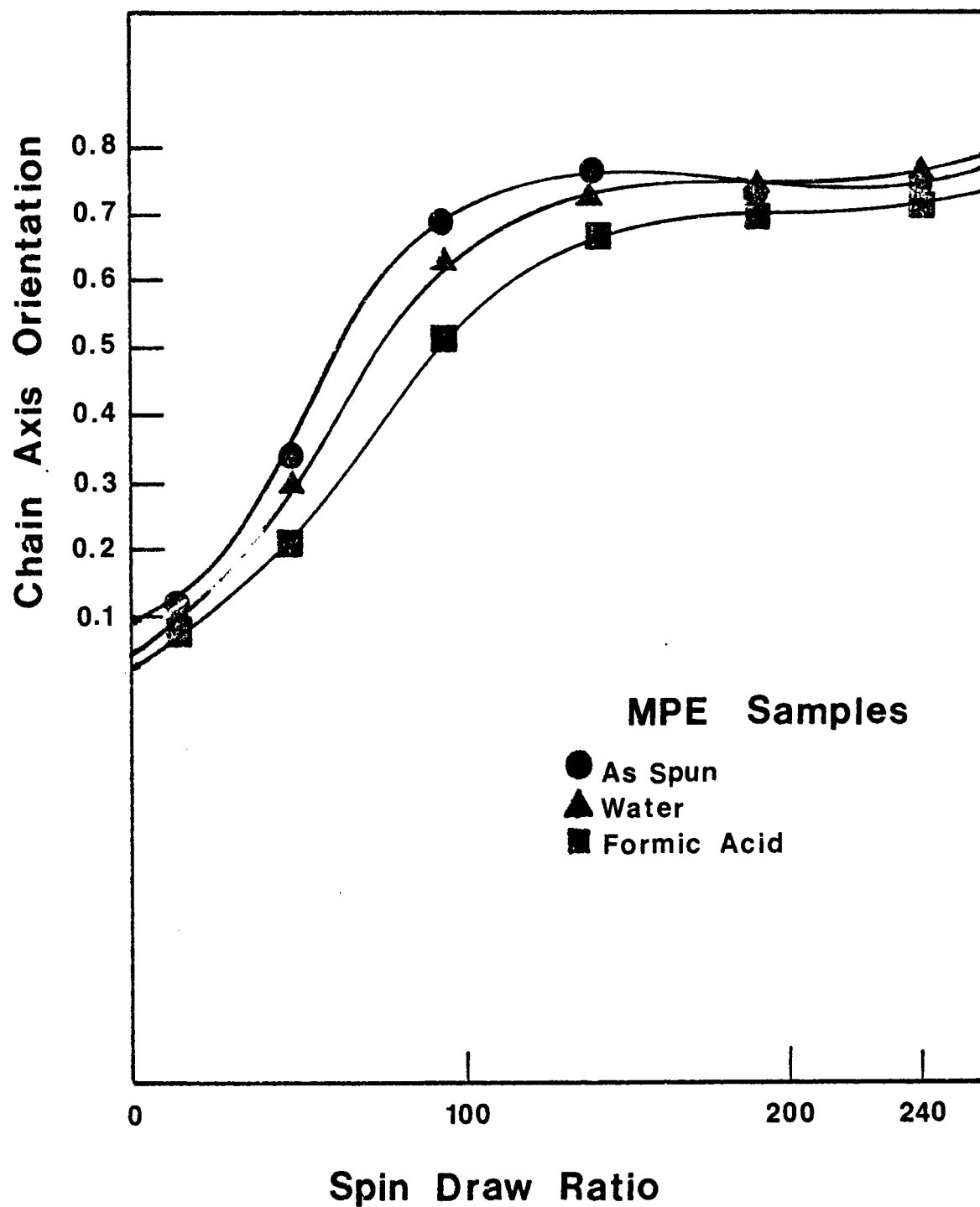


Figure 4.29. Chain Axis Orientation Function of As-Spun and Annealed Samples as a Function of SDR.

crystallinity. One of the most important changes taking place is the perfection of the crystals resulting in a less paracrystalline structure and a larger crystal size.

Parker and Lindenmeyer (73) observed that a single strong equatorial reflection and a strong 020 meridional peak was not sufficient evidence for the existence of γ structure (for existence of parallel hydrogen bonding). Their measurements on the 0, 14, 0 peak of nylon-6 indicates that a meridional reflection at $2\theta = 80^\circ$ is characteristic of the parallel hydrogen bonding of the γ crystal, while an 0, 14, 0 reflection at $2\theta = 77.6^\circ$ is characteristic of anti-parallel bonding (α structure). Figures 4.14, 4.15 and 4.16 show the effect of annealing on the 0, 14, 0 peak of nylon-6. Figure 4.14 shows that annealing a low SDR sample produces no shifting of the peak. This is to be expected since a pseudohexagonal α form is assumed to exist in the as-spun and conditioned filaments spun at low SDR's. Annealing in water of an intermediate SDR sample (Figure 4.15) results in perfection of the crystal structure and formation of a mixture of α and γ crystal structures. This is shown by a split peak at 80° . Annealing in formic acid, however, results in a more predominant α structure and a peak shift to 77.8° . Figure 4.16 shows the effect of annealing a high SDR sample (SDR = 240). In this case, annealing in formic acid causes a shifting of the 0, 14, 0 peak from an as-spun 80° position to 77.8° . The shifting of the peak is characteristic of the shift from γ to α -monoclinic type crystal structure.

The α form produced by annealing in water or partial vacuum is rather imperfect and has been called "paracrystalline α -form" by Roldan and Kaufman (80). This is to be distinguished, however, from

the pseudohexagonal paracrystalline α form assumed to exist in the as-spun and conditioned filaments spun at low SDR's. The d spacings of this monoclinic form are not sharply defined; they vary with the annealing treatment.

The most rapid transformation into the α -form occurs in a 20 percent aqueous formic acid solution. The transformation is slower in water and slowest in vacuum. The rate of transformation increases with temperature in all three media. The annealing in formic acid solution at about 100°C yields an α -form. This result is in agreement with the previous results of Bankar et al. (7). The higher rate of transformation in formic acid is attributed to the ease of breaking the hydrogen bonds by the medium, thus allowing the chains to rearrange themselves. Concentrated formic acid dissolves nylon-6 and this supports this hypothesis.

Figures 4.26, 4.27 show the changes in the α and γ crystalline fractions due to annealing of MPE samples in boiling water or aqueous formic acid. When the as-spun and conditioned filaments are annealed in water or a 20 percent aqueous solution of formic acid, the pseudohexagonal structure (either paracrystalline α or γ) is unstable and tends to change towards the monoclinic α structure. When these changes are analyzed by means of the new γ -index, it becomes clear that while both α -phase content and total crystalline content increase (Figure 4.26), the γ -phase content decreases on annealing. The samples spun at high SDR's retain small amounts of γ -phase even after annealing in boiling formic acid for 2 hours. It may be noted that the chain axis crystalline orientation function is little effected by annealing, Figure 4.29.

CHAPTER V

STRUCTURAL CHANGES DUE TO DRAWING OF MELT SPUN AND CONDITIONED FIBERS

The as-spun and conditioned fibers produced by use of MPE were drawn to different draw ratios. The drawing was done at 90°C on a bench scale apparatus designed and built in our laboratories (9).

Results. Figure 5.1 is a plot of birefringence of as-spun fibers plotted versus draw ratio. The increase in birefringence is rapid at low draw ratios especially for low SDR samples. Figure 5.2 shows the changes in density with draw ratio. The trend is similar to that of the birefringence, although the densities of the as-spun samples do not vary as much as the birefringences. Figure 5.3 shows the changes in the WAXS patterns of a typical nylon-6 as-spun fiber on drawing. On drawing, the single equatorial reflection begins to split into two reflections and the intensity of the meridional reflection diminishes. Figure 5.4 is a similar set of pictures for a low SDR sample. Figures 5.5, 5.6, and 5.7 show diffractometer scans illustrating in a more quantitative way the effect of draw ration on the 002, 202, 200, 020 and 0, 14, 0 reflections of a fast spun nylon-6 sample. Figure 5.8 shows the 0, 14, 0 peak shift due to drawing from an initial value of about 80° for the as-spun (SDR = 240) sample to a value of 77.8° for a sample drawn four times its original length. The low SDR sample has its 0, 14, 0 peak around 78° even in the as-spun condition, Figure 5.9.

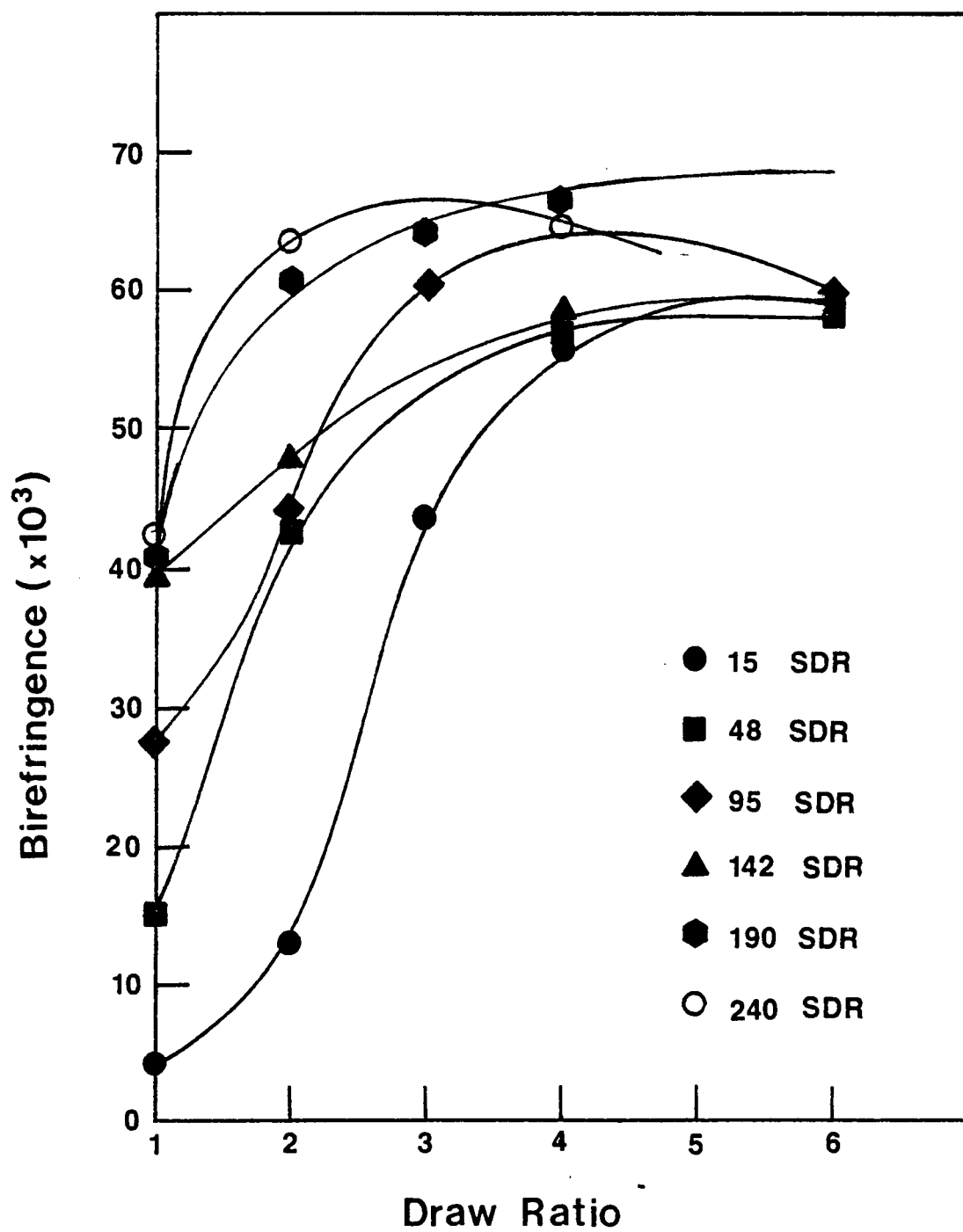


Figure 5.1. Birefringence of As-Spun and Drawn Fibers as a Function of Draw Ratio.

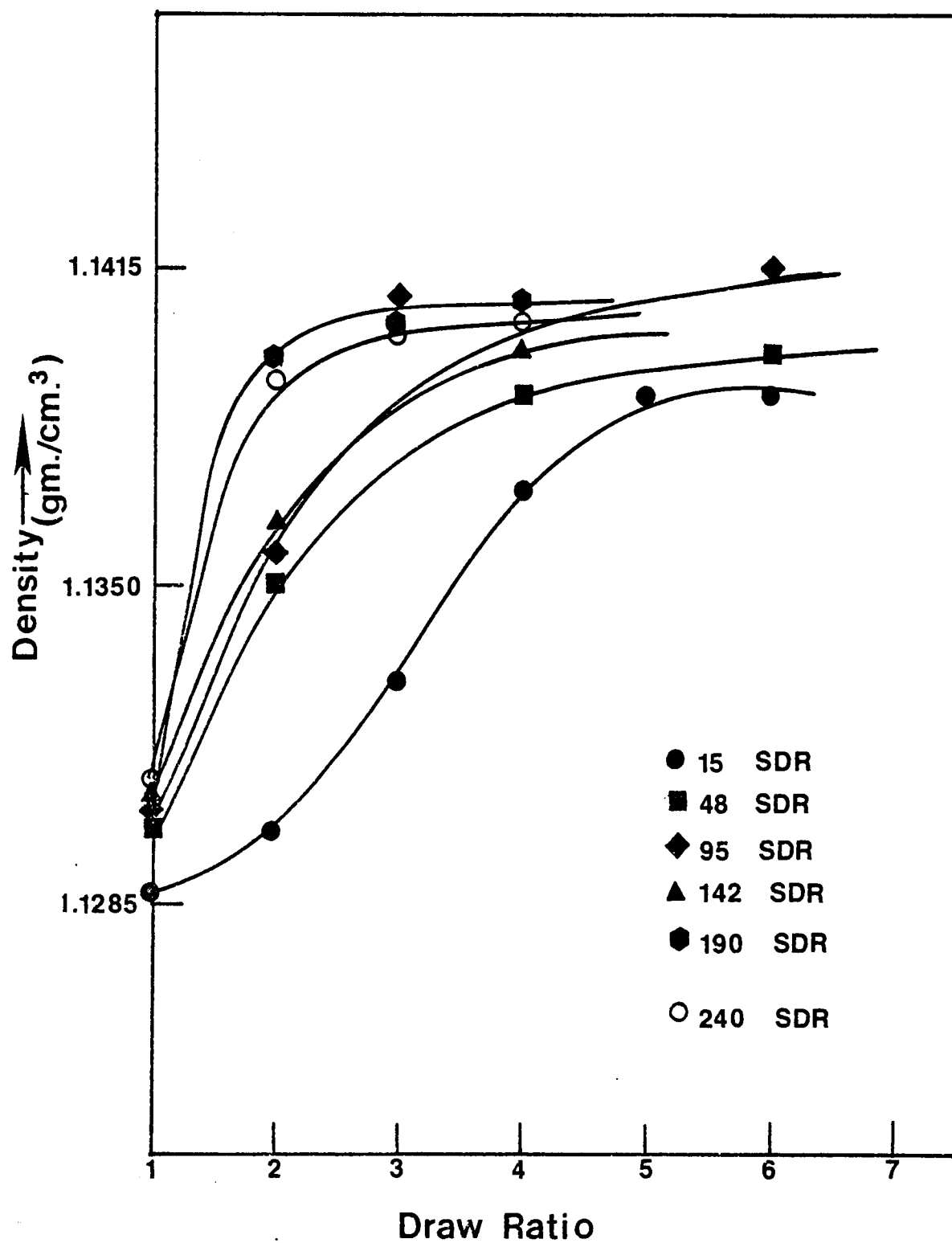
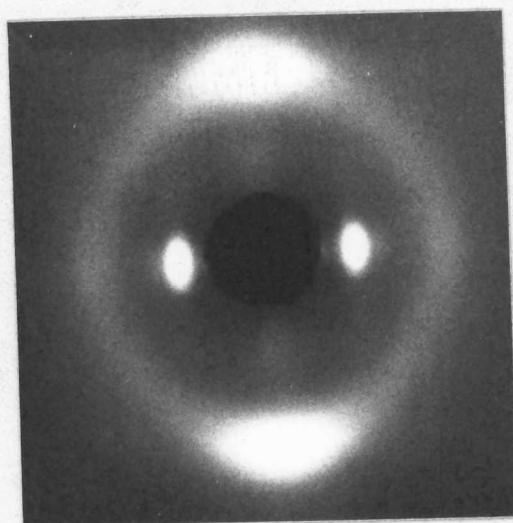
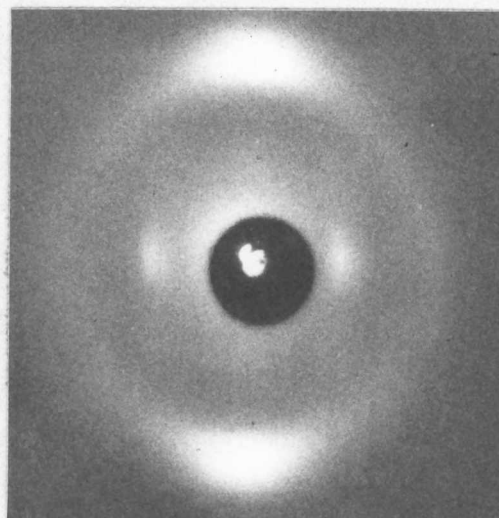


Figure 5.2. Density of As-Spun and Drawn Fibers as a Function of Draw Ratio.

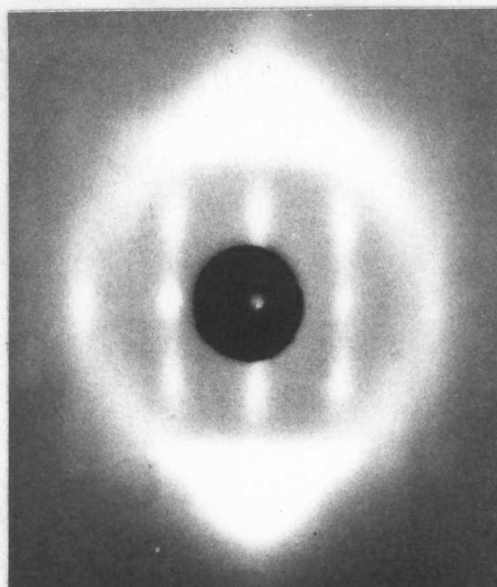
SDR = 142; DRAW TEMPERATURE 90°C



DR = 1



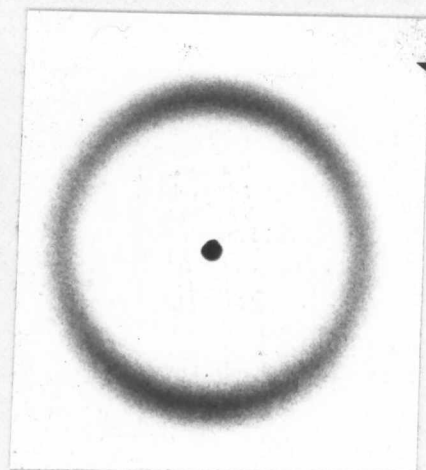
DR = 2



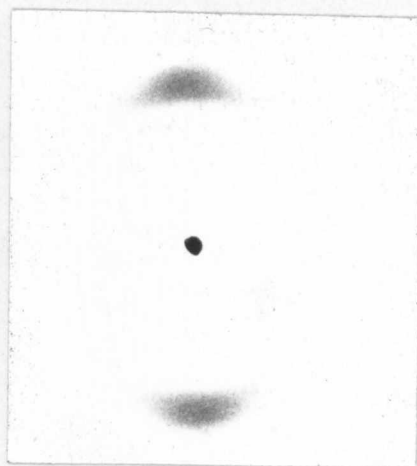
DR = 4

Figure 5.3. WAXS Patterns of Drawn and Conditioned Melt Spun Fibers (SDR 142).

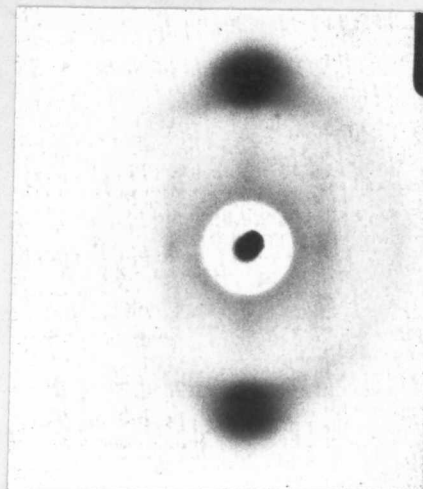
SDR = 15; DRAW TEMPERATURE = 90°C



DR = 2



DR = 3



DR = 6

Figure 5.4. WAXS Patterns of Drawn and Conditioned Melt Spun Fibers (SDR 15).

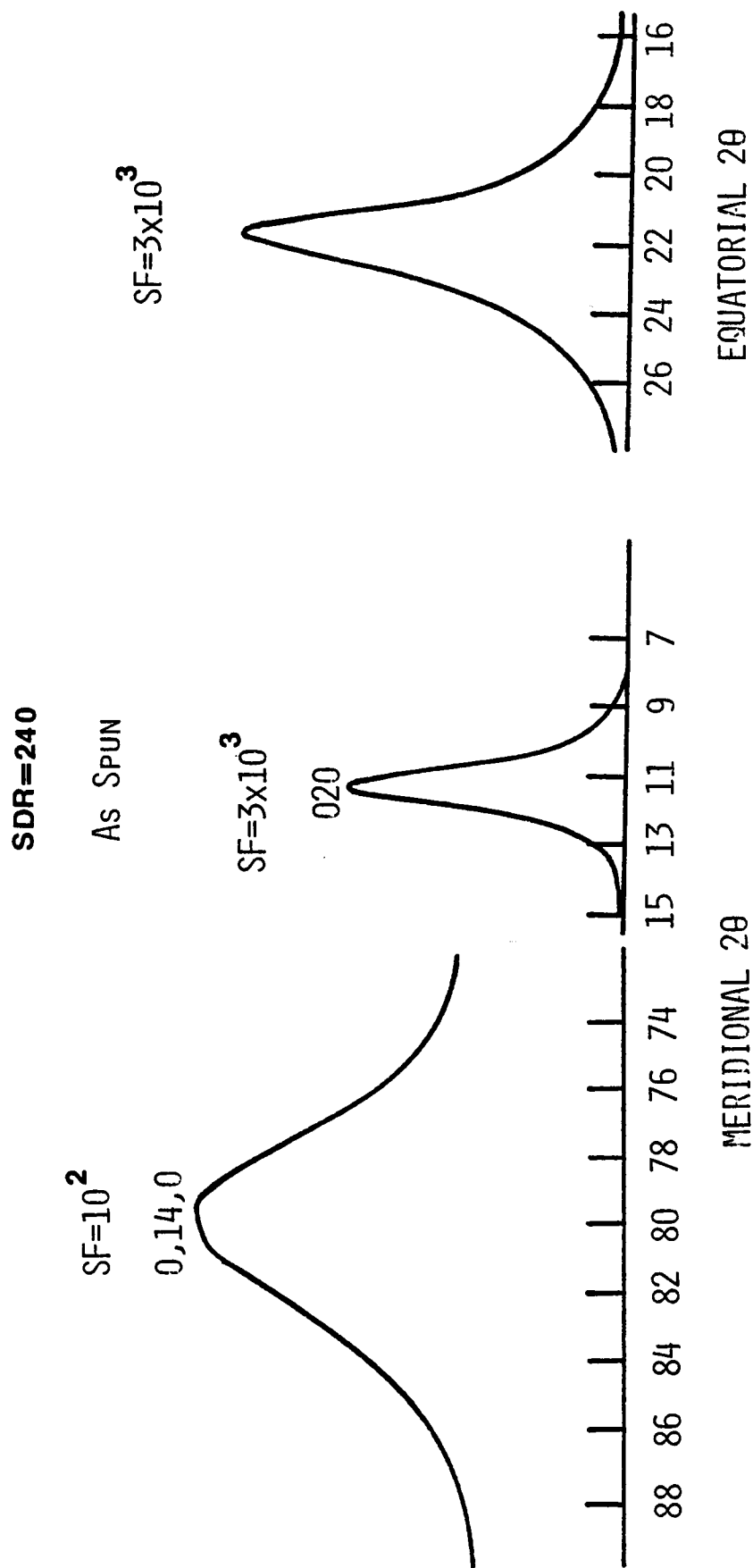


Figure 5.5. WAXS Pattern of As-Spun and Conditioned Filament (SDR 240).

SDR=240
2X DRAW AT 90°C

$SF=3 \times 10^2$

$SF=3 \times 10^2$

$SF=3 \times 10^3$

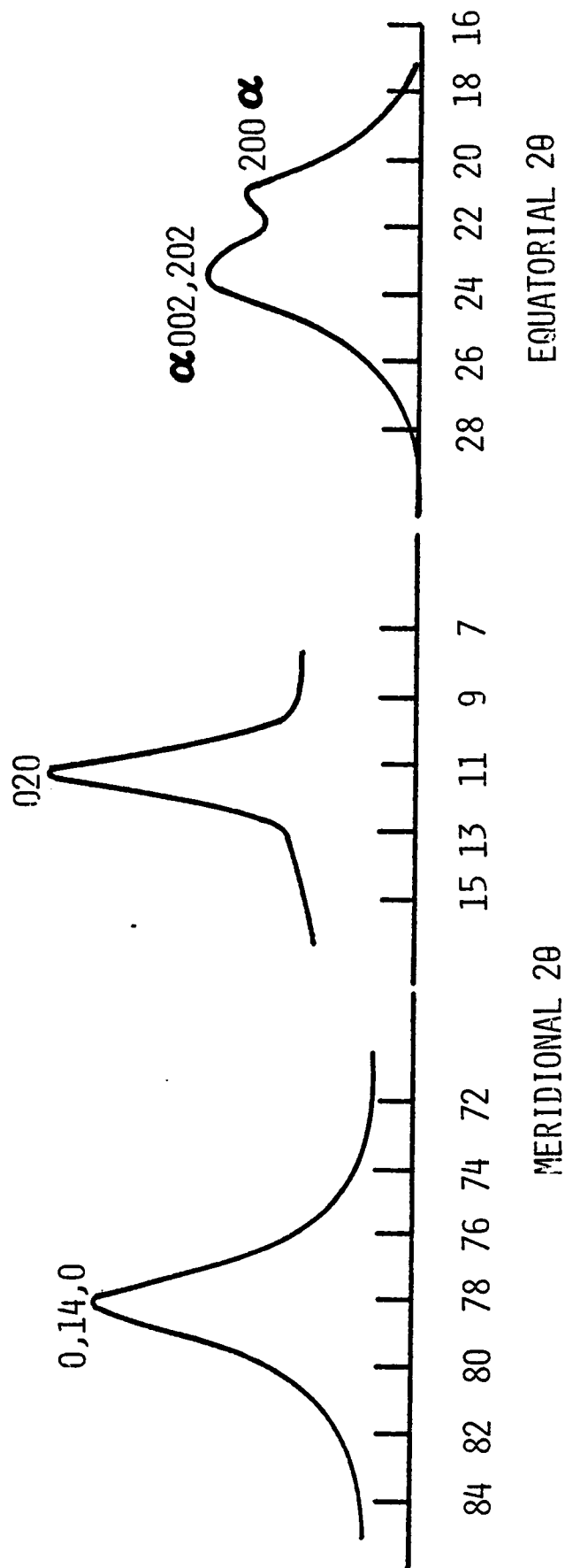


Figure 5.6. WAXS Pattern of As-Spun and Conditioned Filament Drawn 2X at 90°C.

SDR=240

4X DRAW AT 90°C

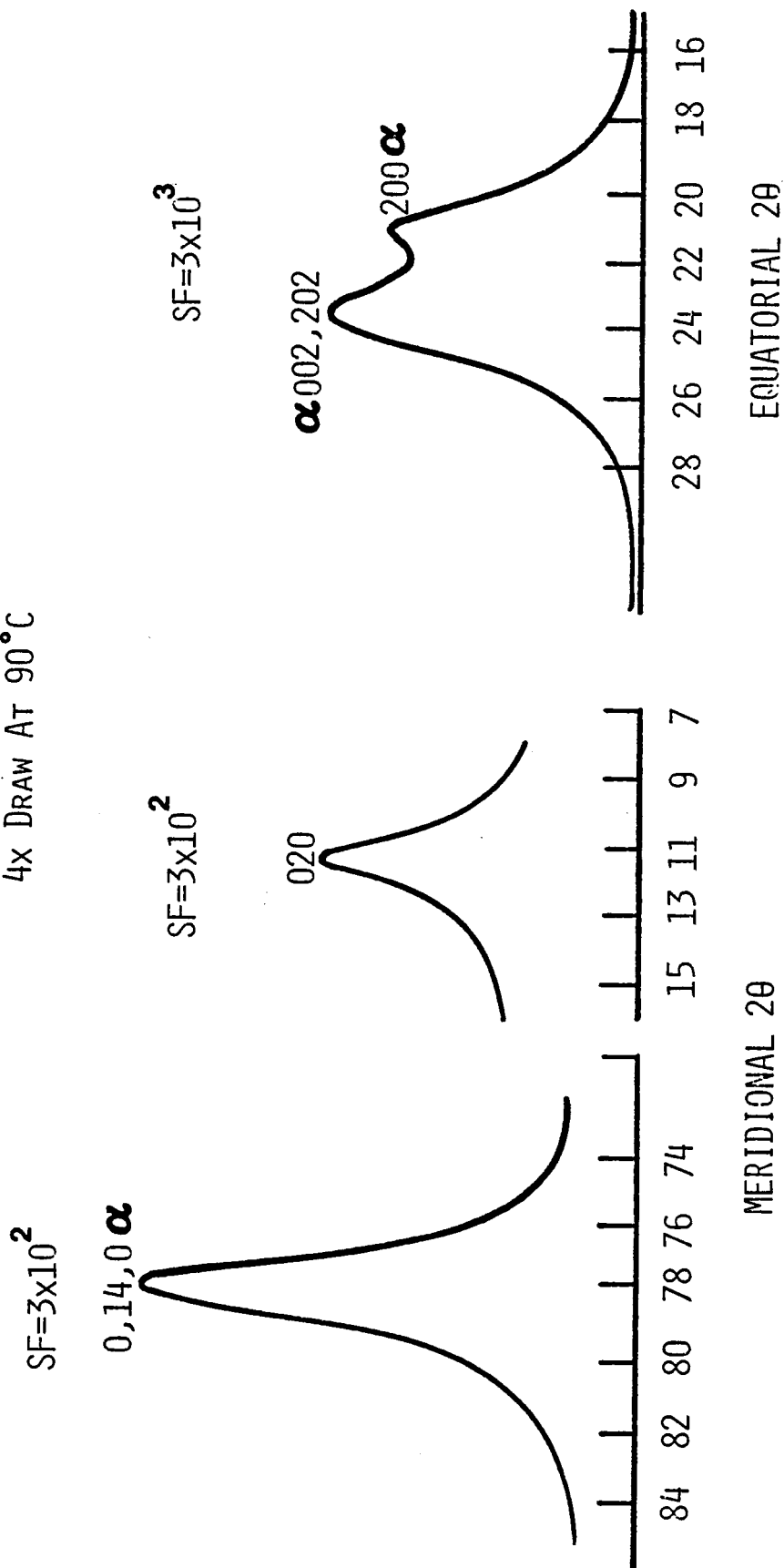


Figure 5.7. WAXS Pattern of As-Spun and Conditioned Filament Drawn 4X at 90°C.

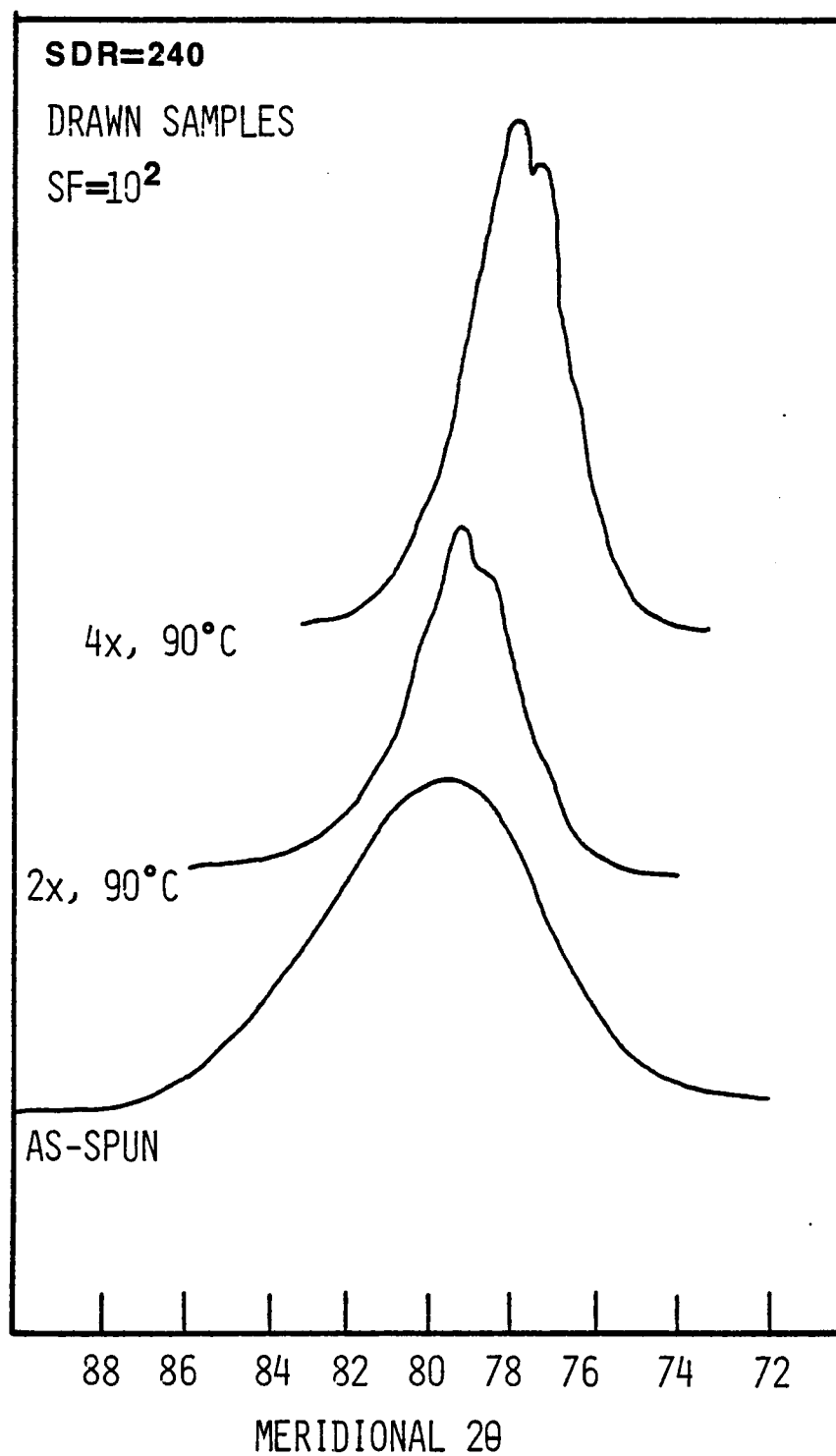


Figure 5.8. Effect of Drawing on 0,14,0 Peak (SDR 240).

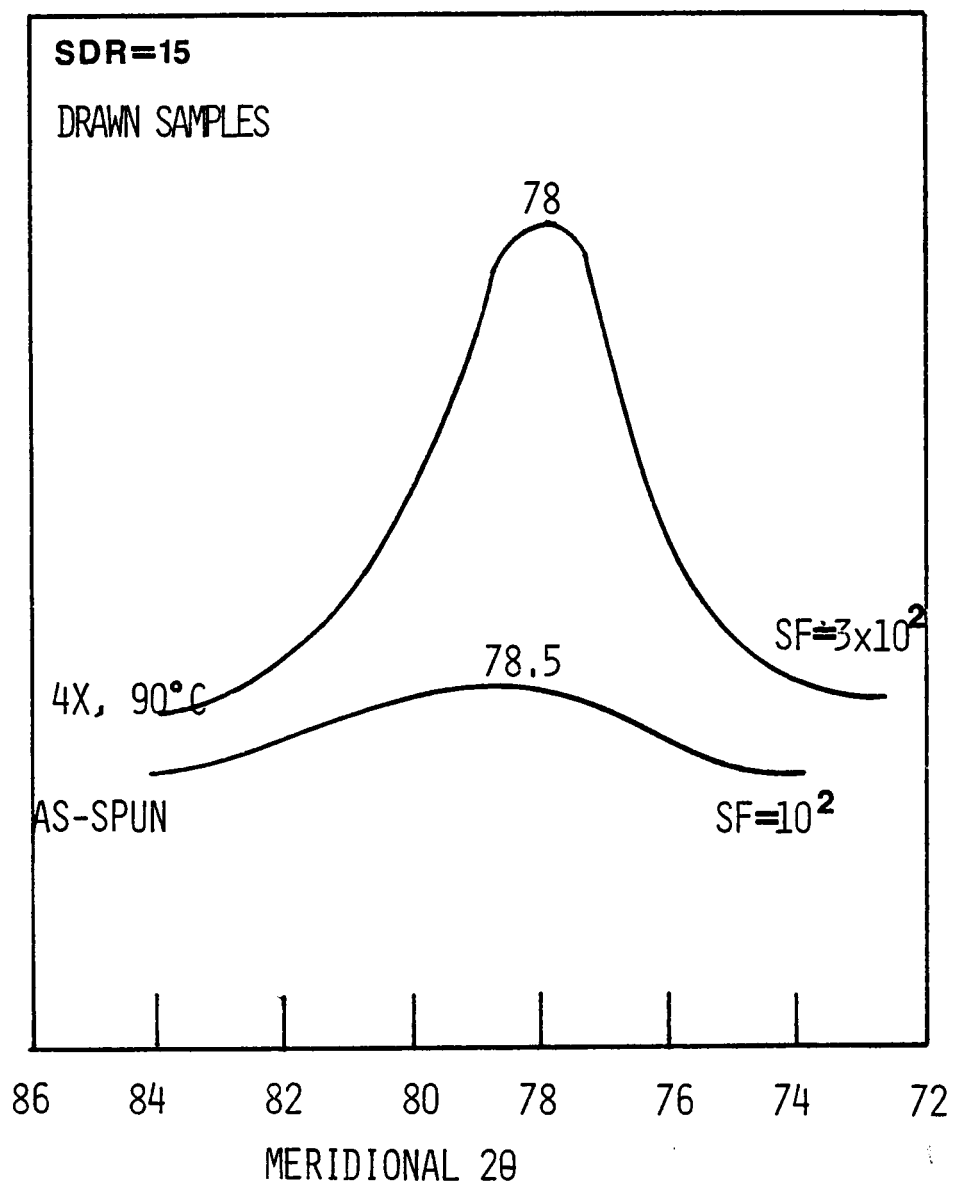


Figure 5.9. Effect of Drawing on 0,14,0 Peak (SDR 15).

Crystallinity indices for drawn filaments were calculated as described in Chapter 3 and are shown in Table VI. Also presented are the density data and crystalline chain axis orientation functions for each sample. Figure 5.10 shows the variation in the two phase fractions α and γ on drawing. The α content increases on drawing; γ content decreases correspondingly. Figure 5.11 shows the changes in the total crystalline fraction on drawing of various spin draw ratios. For lower SDR, the total crystalline fraction increases with draw ratios. For higher SDR, the total crystalline fraction decreases somewhat and then attains a steady value for higher draw ratios.

Figure 5.12 shows the changes in the crystalline chain axis orientation factor with draw ratio. The trend is similar to the data obtained by birefringence. Figure 5.13 shows the changes in f_{am} , the amorphous chain orientation factor with draw ratio. The result was computed assuming that all the drawn samples are primarily α -phase.

Discussion. Figure 5.1 shows the changes in birefringence with draw ratio. The increase in birefringence is rapid at low draw ratios. Beyond a certain draw ratio, the birefringence attains a steady value. In general, higher SDR samples exhibit higher values of birefringence. This indicates that for a given extension samples with higher SDR values show higher levels of average molecular orientation. The density data (Figure 5.2) indicates that the overall crystallinity increases with draw ratio. The increase in density and hence crystallinity is more rapid at low draw ratios. Higher SDR samples generally exhibit higher density values for a given extension. The WAXS data of Figures 5.3 through 5.8 appear to be consistent with development of an increased fraction of the α monoclinic crystal

TABLE VI
VARIOUS PHASE FRACTIONS OF AS-SPUN AND DRAWN FILAMENTS OF NYLON-6

Spin Draw Ratio	γ Fraction	α Fraction	Total Crystalline Fraction	Amorphous Fraction	Density	Chain Axis Orientation
15	.022	.341	.363	.637	1.1288	.07
2x	.015	.353	.369	.631	1.1300	.27
4x	.002	.410	.412	.588	1.1370	.74
48	.043	.337	.380	.620	1.1301	.20
2x	.032	.378	.410	.591	1.1350	.74
4x	.014	.415	.430	.570	1.1389	.85
142	.245	.211	.456	.544	1.1303	.66
2x	.054	.373	.427	.573	1.1363	.77
4x	.019	.419	.438	.562	1.1399	.80
6x	.007	.431	.438	.562	1.1405	—
240	.254	.213	.467	.533	1.1315	.71
2x	.037	.404	.441	.559	1.1393	.80
4x	.020	.423	.442	.557	1.1405	.82
6x	.005	.435	.441	.559	1.1410	—

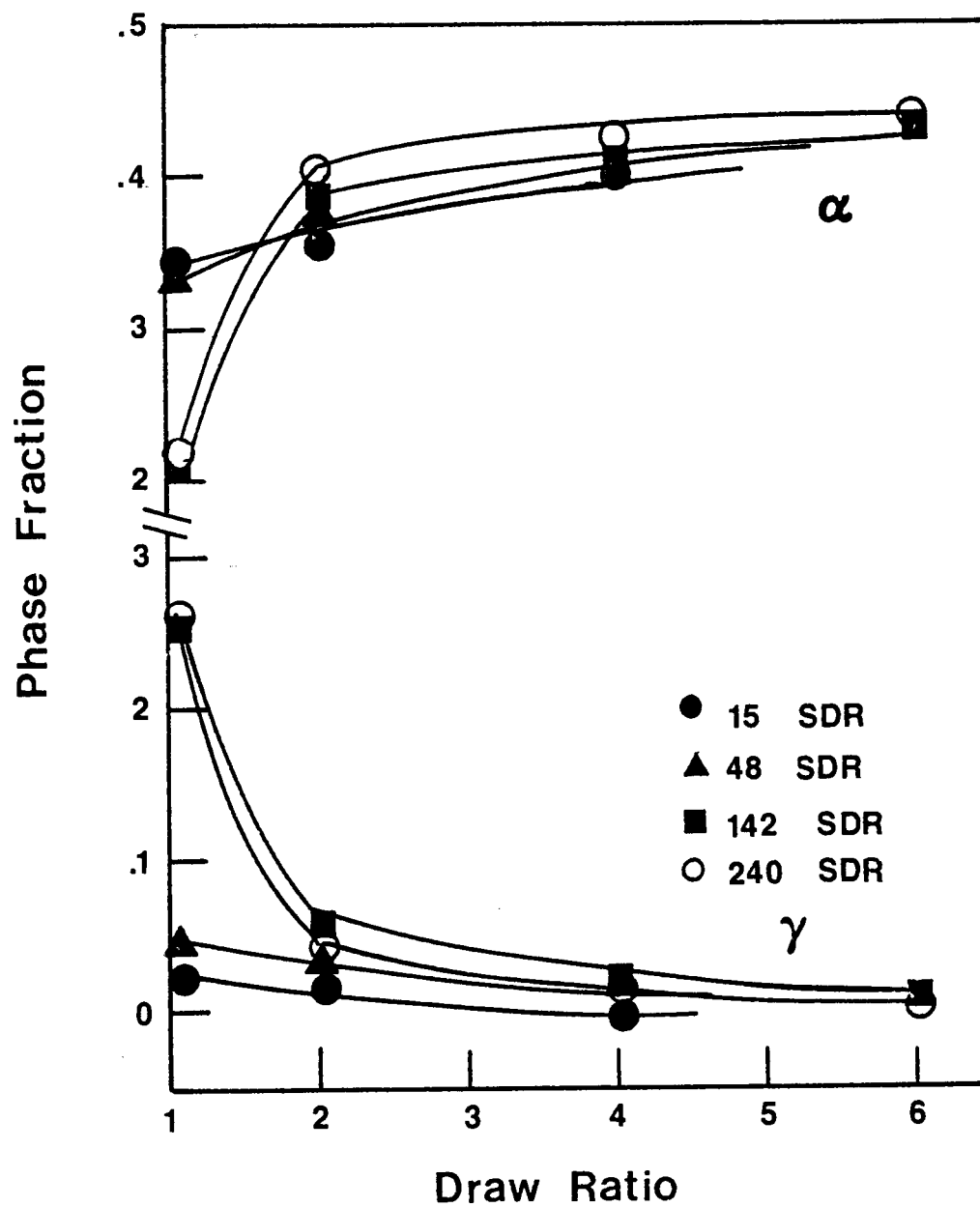


Figure 5.10. Various Phase Fractions of Nylon-6 as a Function of Draw Ratio.

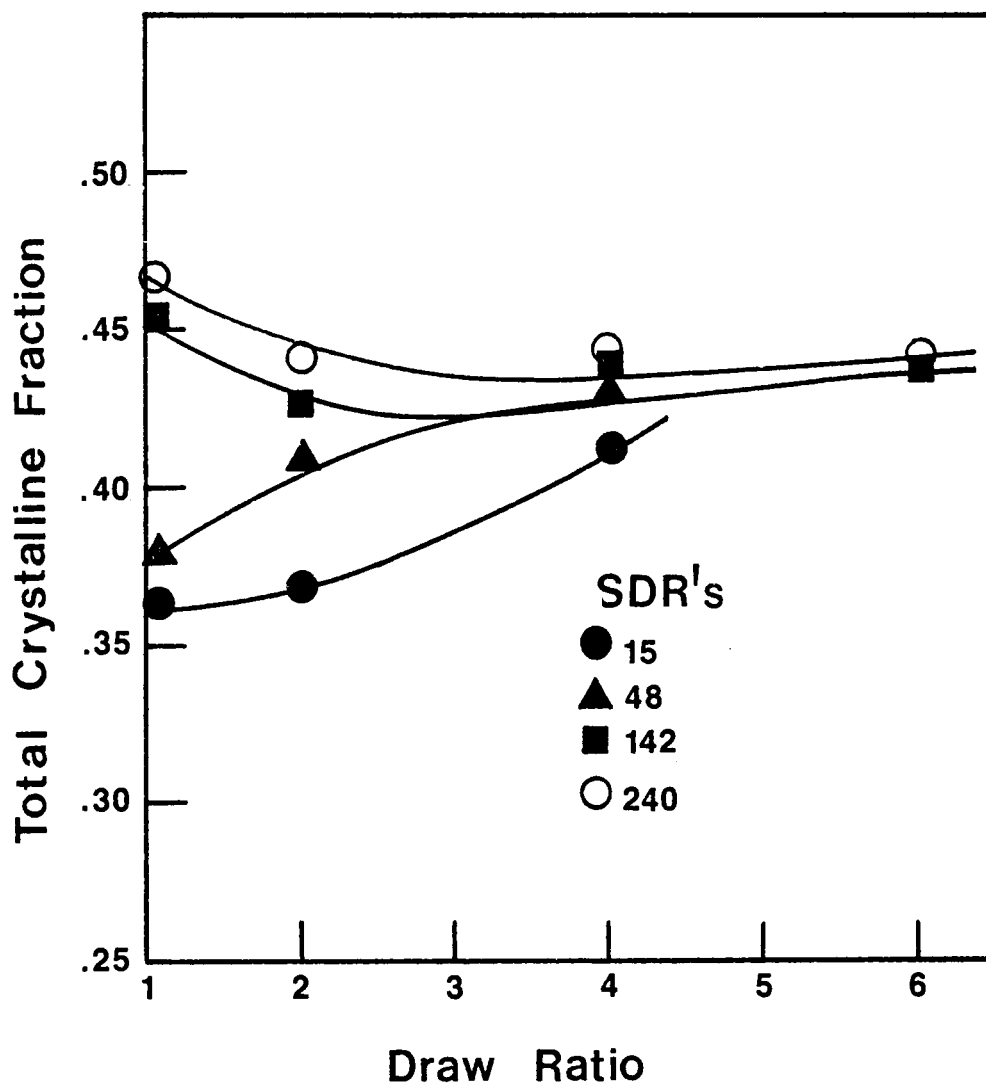


Figure 5.11. Total Crystalline Fraction as a Function of Draw Ratio.

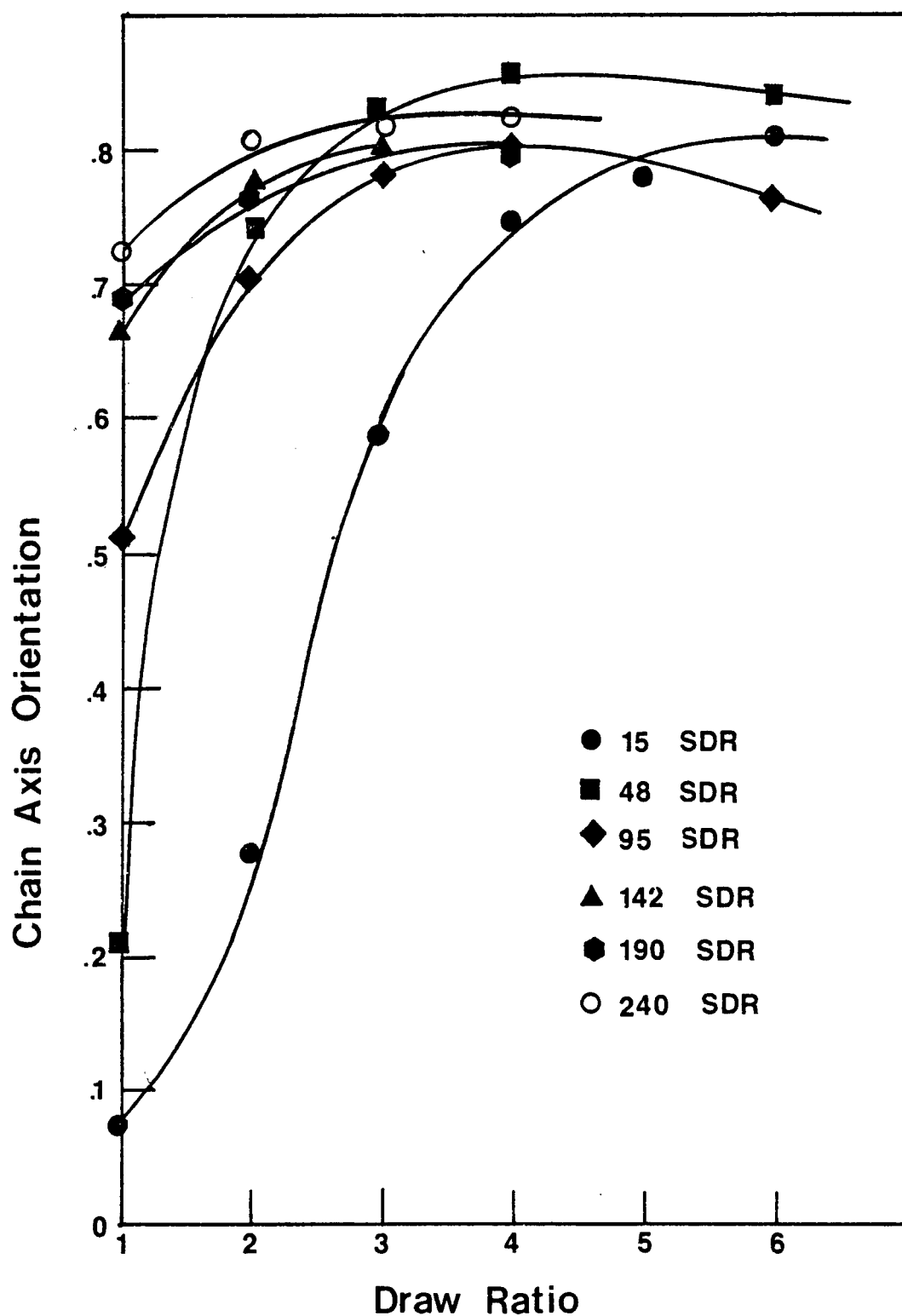


Figure 5.12. Chain Axis Orientation Function of As-Spun and Drawn Fibers as a Function of Draw Ratio.

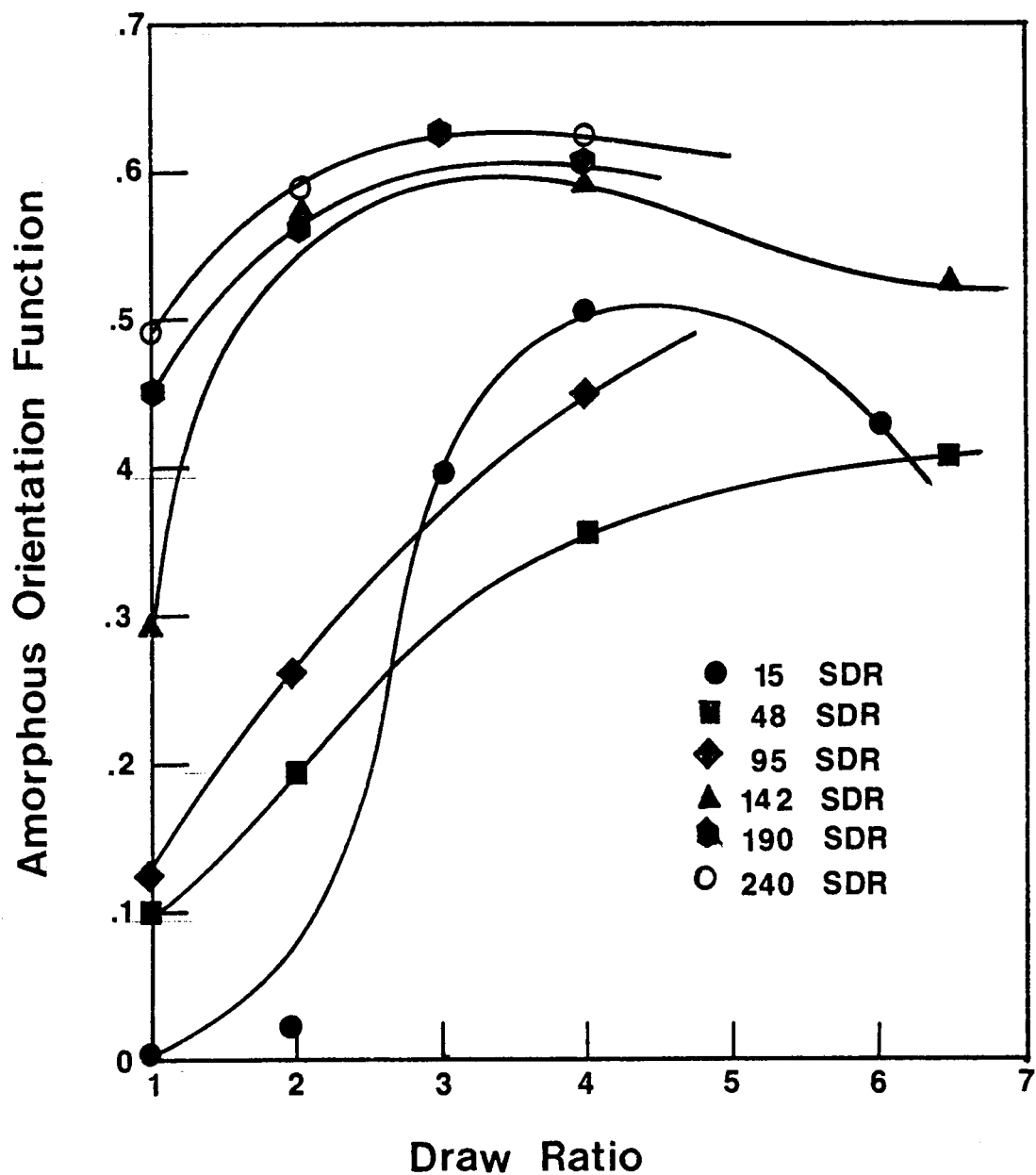


Figure 5.13. Amorphous Orientation Function of Nylon-6 as a Function of Draw Ratio.

structure during drawing. The formation of the α monoclinic phase causes the splitting of the equatorial reflections, diminishing of the meridional intensity and a shift in the position of the 0, 14, 0 reflection. These changes observed are similar to those previously described for annealing of the as-spun filaments in water or formic acid, although the α -phase produced by drawing does not seem to exhibit the degree of perfection that can be achieved by annealing in formic acid.

Figure 5.10 shows the variation in the two crystalline phase fractions α and γ on drawing. Drawing increases the α -phase content and decreases the γ -phase content. The total crystalline content increases with draw ratio for samples spun with low SDR's, but drawing has little effect on the total crystalline content of samples spun with higher SDR's as shown in Figure 5.11. Drawing also results in substantial increases in orientation, especially for the samples spun at low SDR's.

Changes in the crystalline orientation function f_c , (Figure 5.12) follow the same trend as the birefringence, Figure 5.1. The chain axis orientation of the crystals increases with increasing draw ratio. For a given extension, samples with higher SDR values show higher crystalline orientation function. The results in Figure 5.13 show increasing amorphous orientation at draw ratios up to 2-3X. The results in Figure 5.13 need to be considered carefully, and cannot be used to quantitatively describe f_{am} , the amorphous orientation function.

Not much data is available in the literature on the drawing behavior of nylon-6. Stepaniak et al. (98) have reported on changes in the crystal structure and crystallinity on drawing of nylon-6. They

conclude that the drawing or annealing of nylon-6 fibers produces a crystal structure high in the α -component. They also conclude that drawing of conditioned as-spun filaments results in appreciable increase in the overall crystallinity, this effect increasing with draw ratio and draw temperature. More significantly they report the proportions of the α and γ components also change with drawing. Our results are in general agreement with their agreement with their conclusions.

However, our results based on the γ -index are not in quantitative accord with their results. In contrast to their results, our data shows that the crystallinity increases on drawing only for low SDR samples and in fact decreases for high SDR samples. The results of Stepaniak et al. (98) are based on a different method of obtaining the γ fraction.

CHAPTER VI

TENSILE PROPERTIES OF MELT SPUN FILAMENTS AND DRAWN FIBERS

Results for As-spun and Conditioned Fibers. Typical engineering stress-elongation data for the as-spun and conditioned filaments are shown for different SDR's in Figure 6.1. The values of tensile strength, Young's modulus and elongation to break extracted from these curves are plotted in Figure 6.2 , 6.3 , and 6.4.

Results for Drawn Fibers. Figure 6.5 shows typical engineering stress-elongation data for drawn nylon-6 fibers having an original SDR of 48. Data for different SDR's extracted from such curves are plotted in Figures 6.6, 6.7 and 6.8. Figure 6.6 shows the effect of draw ratio on the tensile strength of nylon-6. Figure 6.7 shows the variation of Young's modulus as a function of draw ratio.

Discussion of As-spun Filaments. The stress-strain behavior of nylon-6 filaments is in agreement with the previous work of Bankar (8). Figures 6.1 and 6.2 show the tensile strength and the modulus increasing with increasing SDR. The elongation to break decreases with increasing SDR. Figure 6.1 also shows a distinct yield point for the low SDR samples. Such a yield point is not observed for fibers spun at very high SDR (150 and above). In earlier studies (18, 19, 113), spinline stress was shown to be the primary variable in determining the morphology and physical properties of spun polyethylene and polypropylene fibers. Bankar (7) plotted tensile properties of nylon-6 against spinline stress and take-up velocity. It should be noted that the properties of

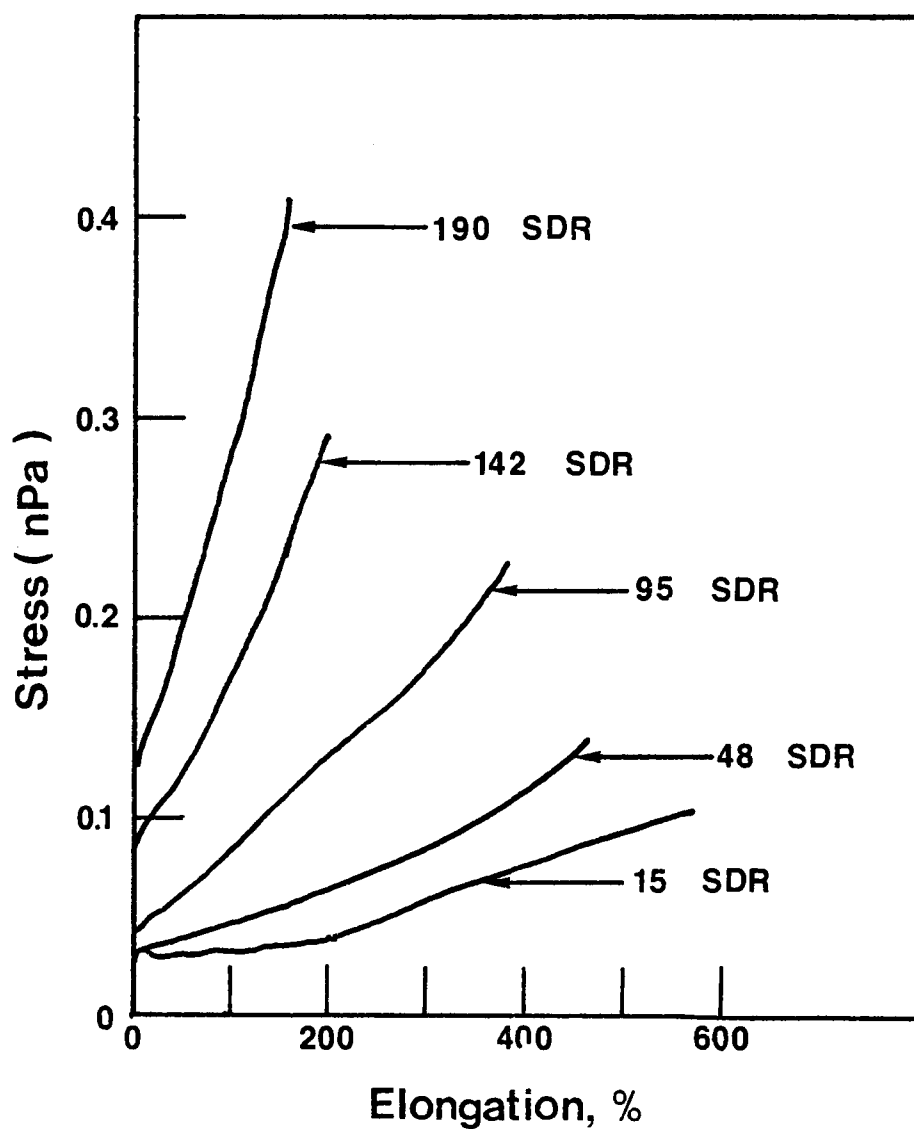


Figure 6.1. Engineering Stress Versus Elongation of Nylon-6 Fibers Spun at Various SDR's.

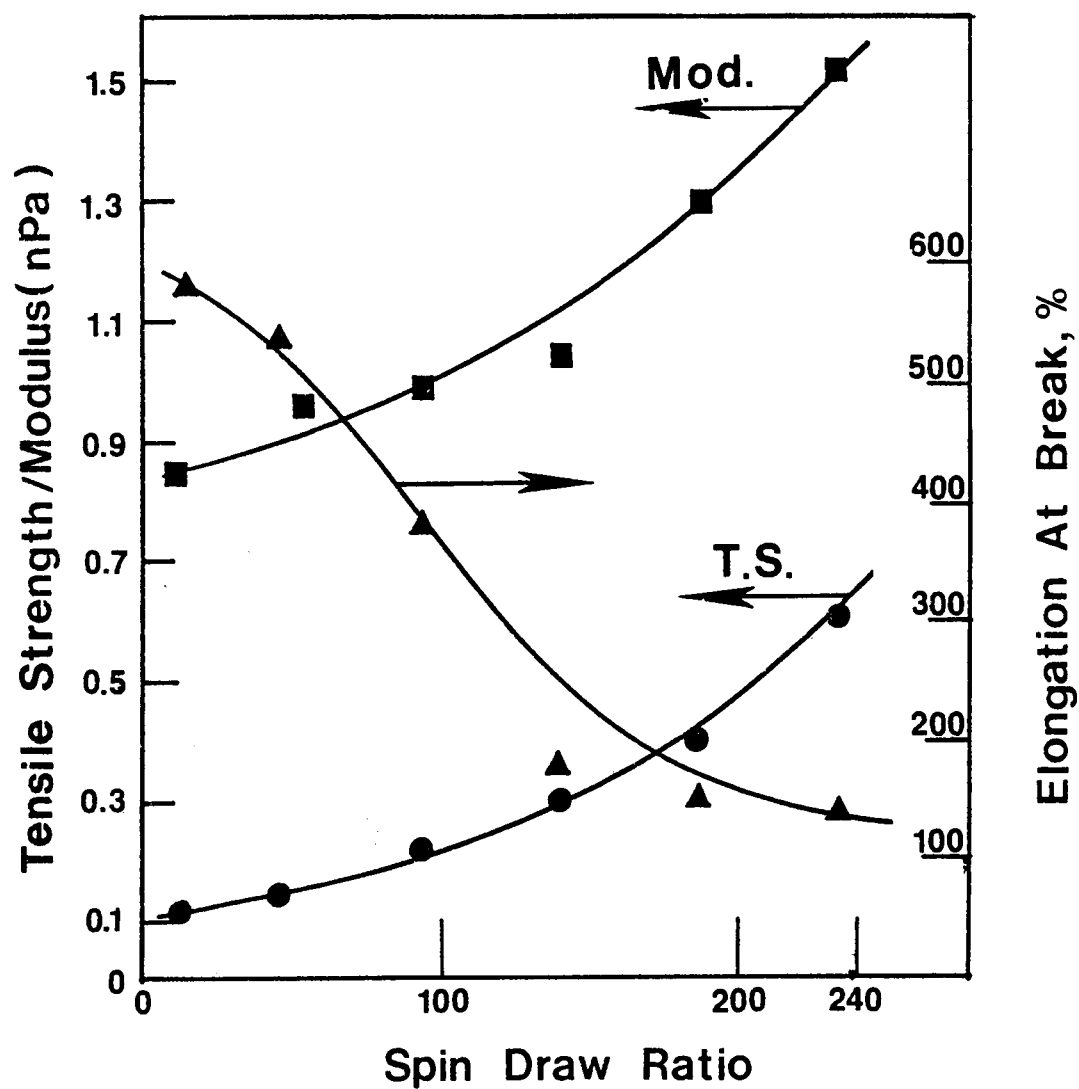


Figure 6.2. Tensile Properties of Nylon-6 as a Function of SDR.

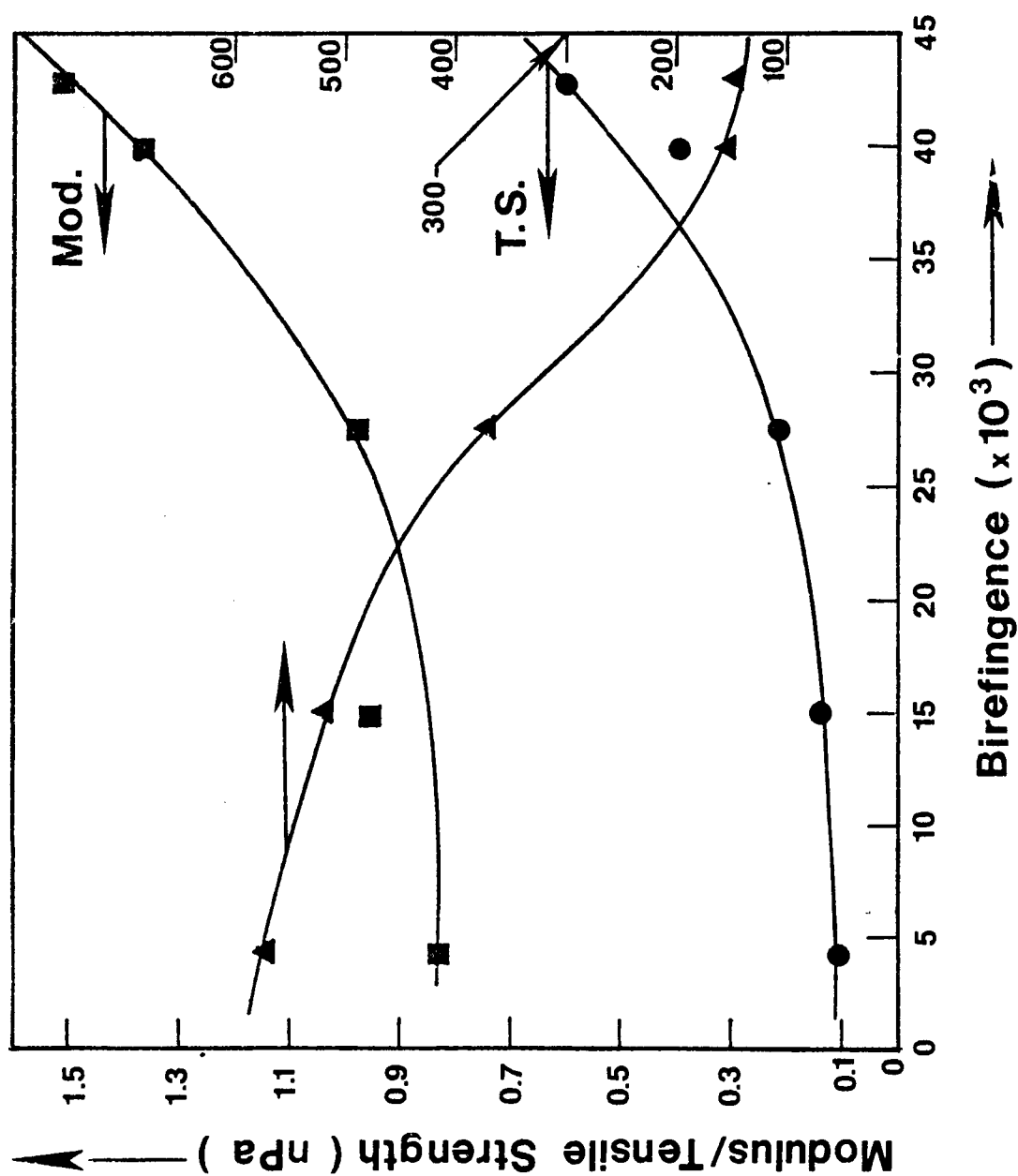


Figure 6.3. Tensile Properties of Nylon-6 as a Function of Birefringence

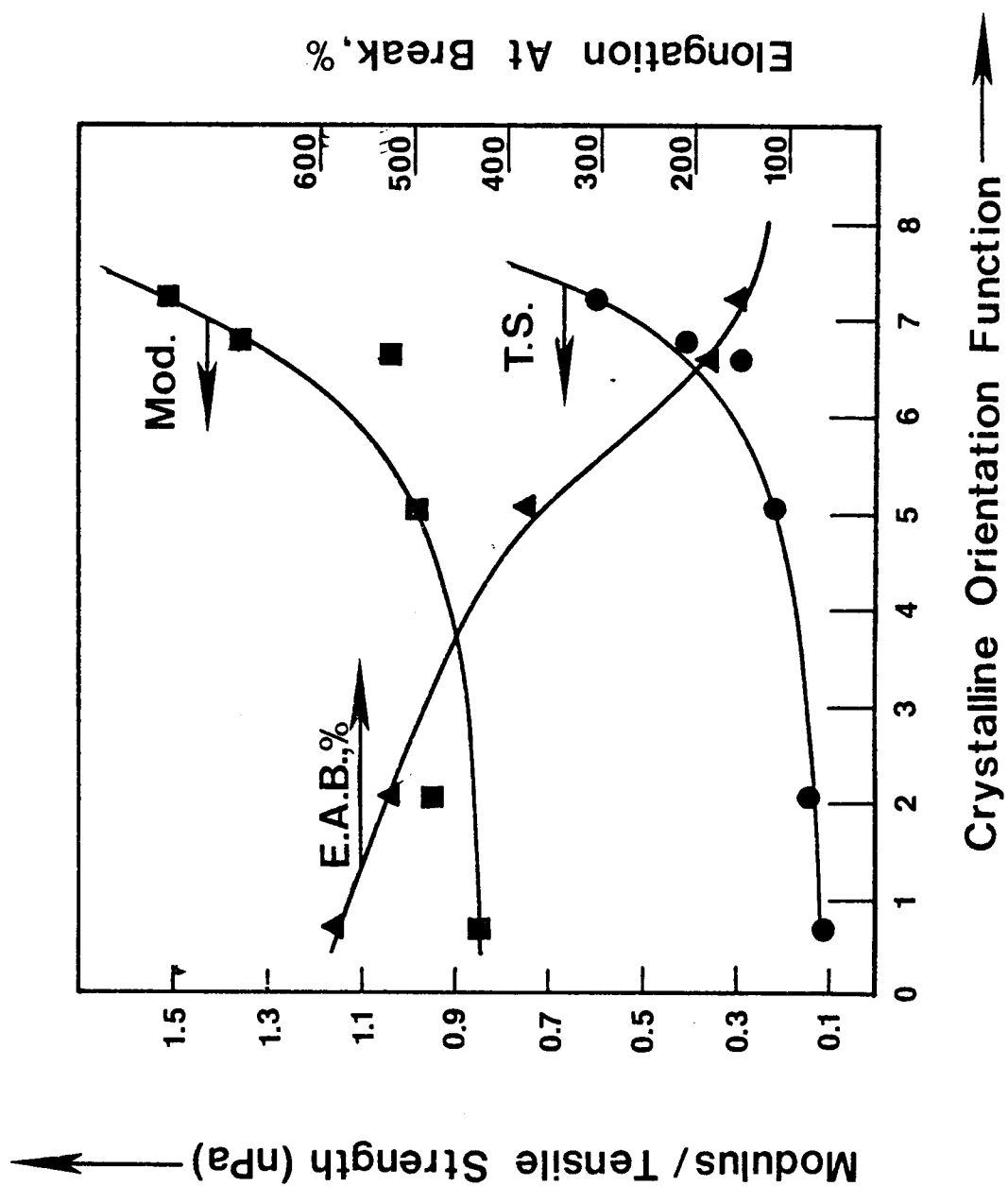


Figure 6.4. Variation of Tensile Properties with Crystalline Orientation Function.

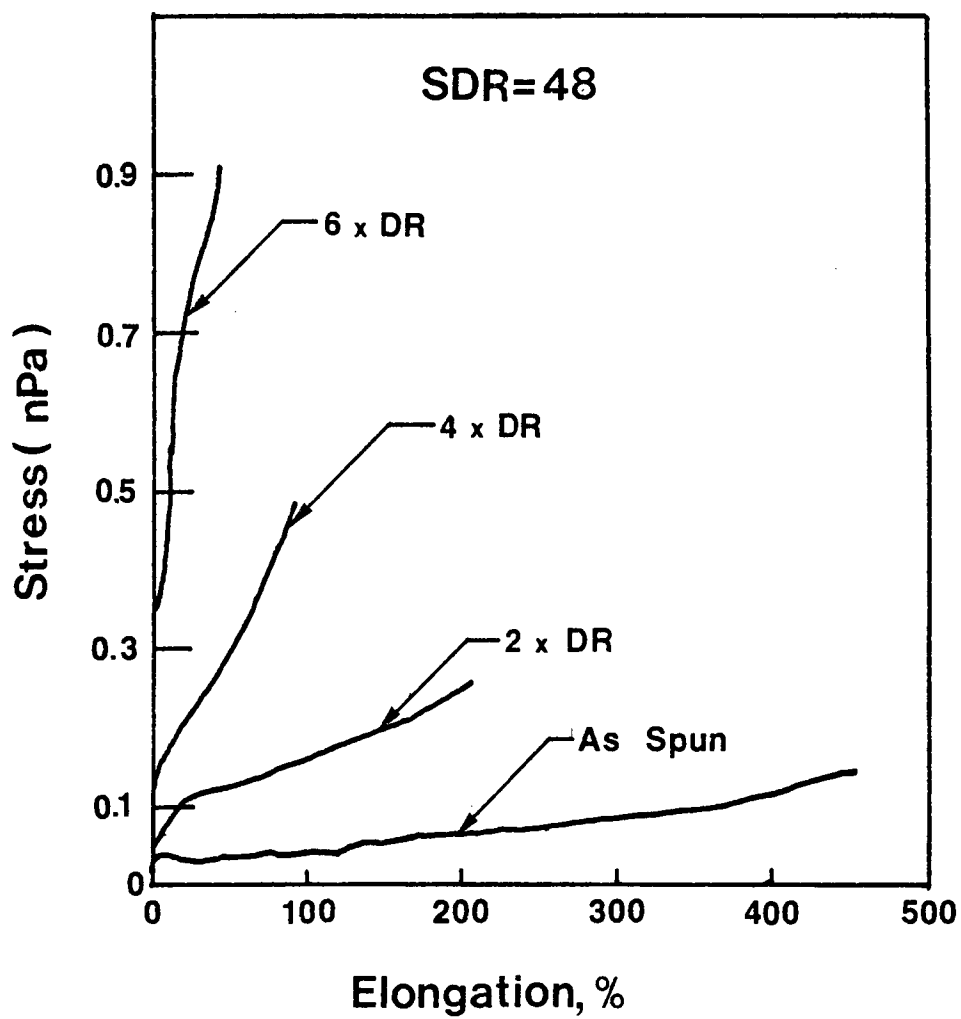


Figure 6.5. Engineering Stress Versus Elongation of Nylon-6 Fibers Drawn to Various Draw Ratios.

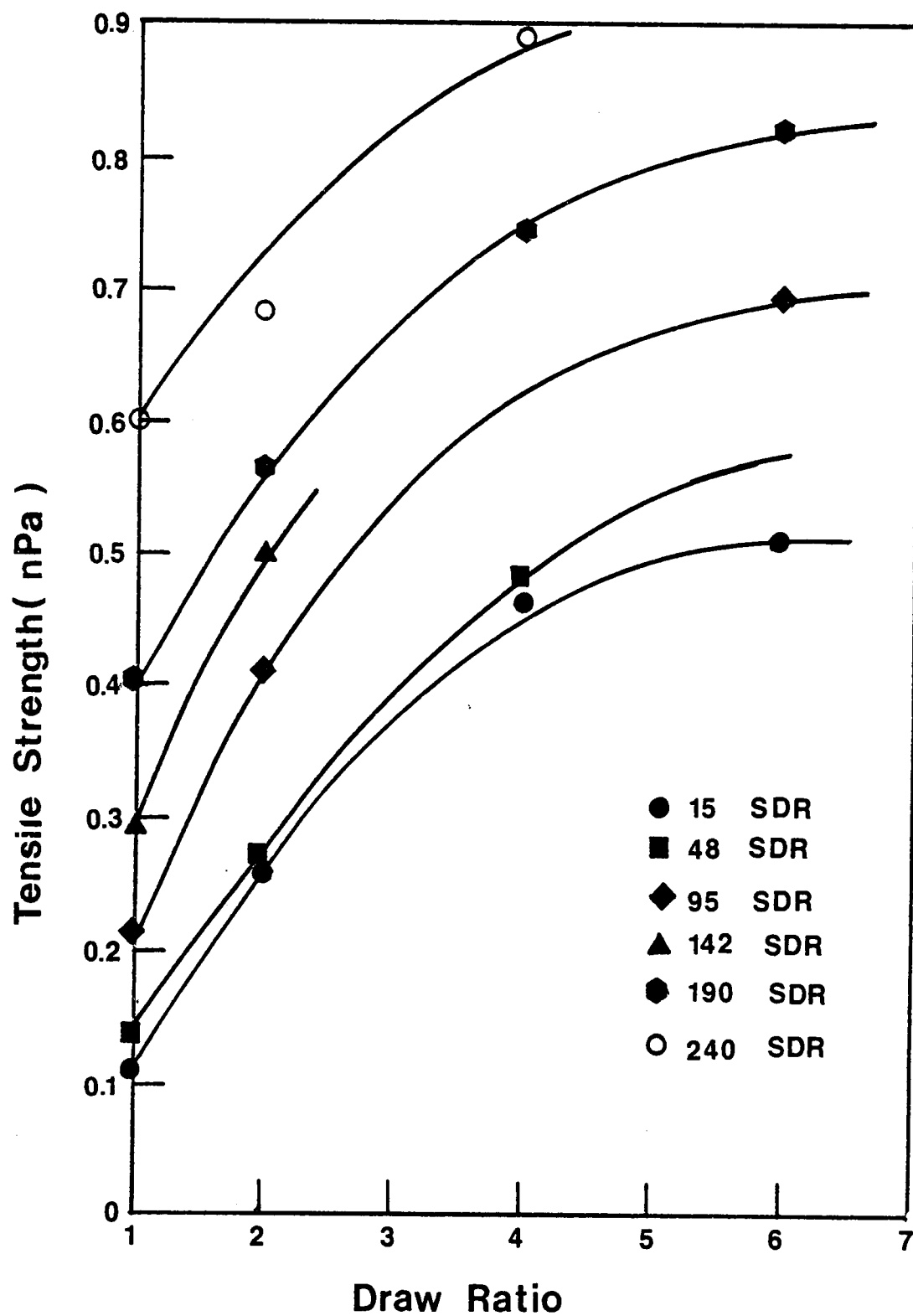


Figure 6.6. Tensile Strength of Nylon-6 as a Function of Draw Ratio.

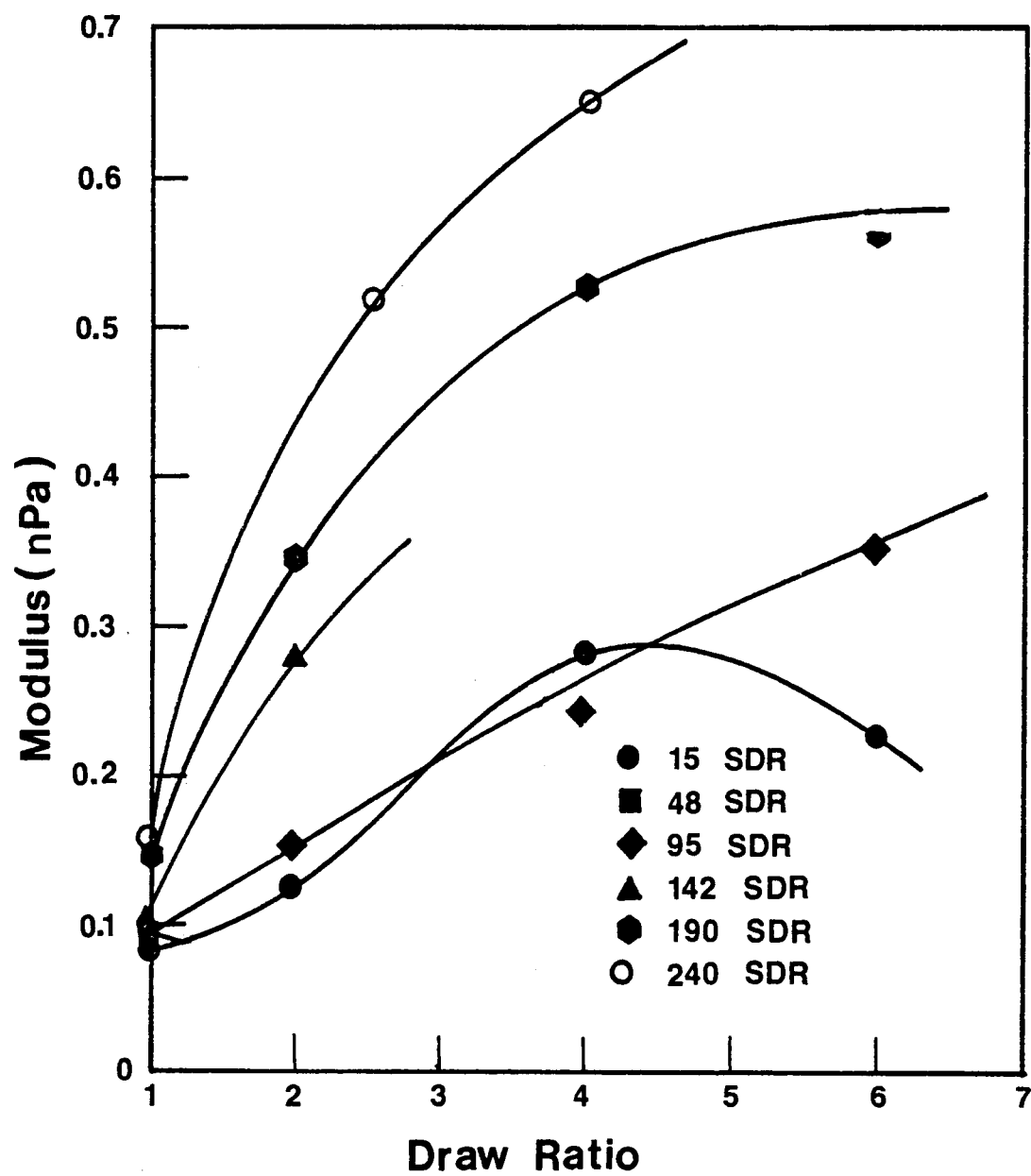


Figure 6.7. Modulus as a Function of Draw Ratio.

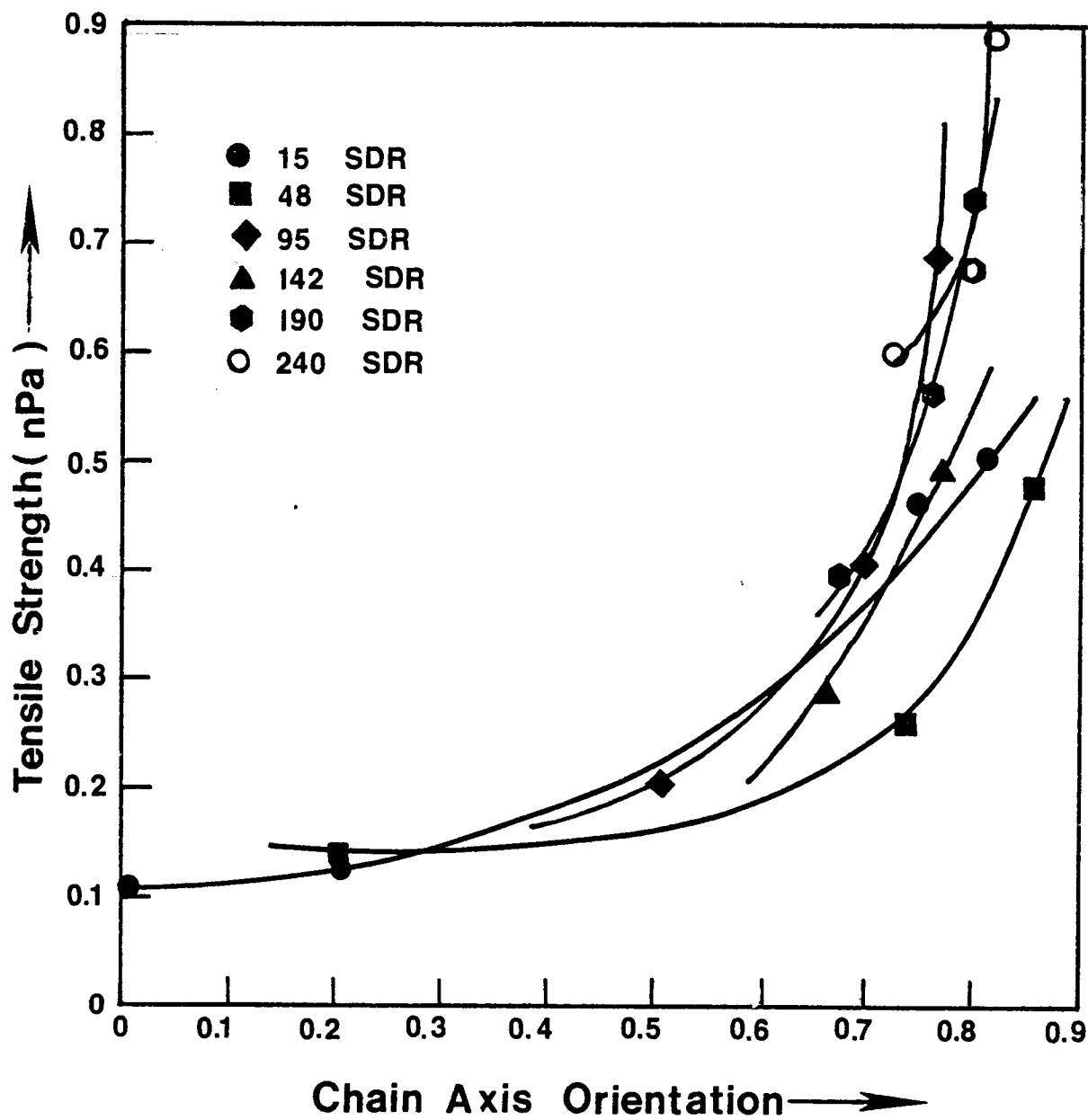


Figure 6.8. Tensile Strength as a Function of Chain Axis Orientation

nylon-6 vary in the same general manner with the spinline stress, take-up velocity and SDR. Figures 6.3 and 6.4 show that the tensile strength and Young's modulus increase slowly with birefringence and c-axis crystalline orientation factor f_c . The increase is much sharper in the regions of high values of birefringence and f_c .

Discussion of Drawn Fibers. Figures 6.4 and 6.5 show that the tensile strength and Young's modulus increase with increasing draw ratio. Several researchers (60, 92, 117) have correlated the tensile properties of spun fibers with the chain axis crystalline orientation function. Samuels (84) studying drawn polypropylenes used average and amorphous orientation factors. He suggested that the state of orientation and not the fabrication draw ratio should be used to characterize the mechanical properties of fibers and films. White et al. (108) observed that in drawn polyethylene fibers the tensile strength and modulus increase by a factor of about ten over the melt spun fibers.

Figure 6.8 shows how the tensile strength varies with the chain axis crystalline orientation function. It is seen that at high values of crystalline orientation the tensile strength is very sensitive to the chain axis crystalline orientation. As was discussed in Chapter 5, crystallinity, birefringence and density attain steady values at high draw ratio. Figure 6.7 shows a general trend of increasing modulus with increasing draw ratios. An interesting observation is that the tensile strength and modulus increase with increasing draw ratio even when the crystallinity and birefringence attain steady values. Hence it is evident that the fiber properties like tensile strength do not solely depend on the degree of crystallinity, or the crystalline orientation. The increase in tensile strength at high draw ratios

could be attributed to changes in the amorphous orientation of the filament. Slight increases in the amorphous orientation at high draw ratios could cause an appreciable increase in the tensile strength of the fiber.

SAXS and diffusion studies have shown that the interfibrillar domains play an important role in fibers for mechanical properties. This certainly seems to be the case here. To better understand the correlation of mechanical properties with structure, one needs to study the structural model of nylon-6.

Structural Model for Nylon-6

A frequently suggested correlation is given by Samuels (84) for polypropylene, and it involves the relationship between amorphous orientation functions and fiber modulus, strength and coefficient of diffusion. It has been shown by Prevorsek et al. (76) that a structural model consisting of crystallites embedded in an amorphous matrix yields better results than a microfibrillar model assuming relatively poor lateral interactions between the microfibril for nylon-6. The most important consequence of this finding is that the fiber properties do not depend on the degree of crystallinity but also on the dimensions and spacings between the crystallites.

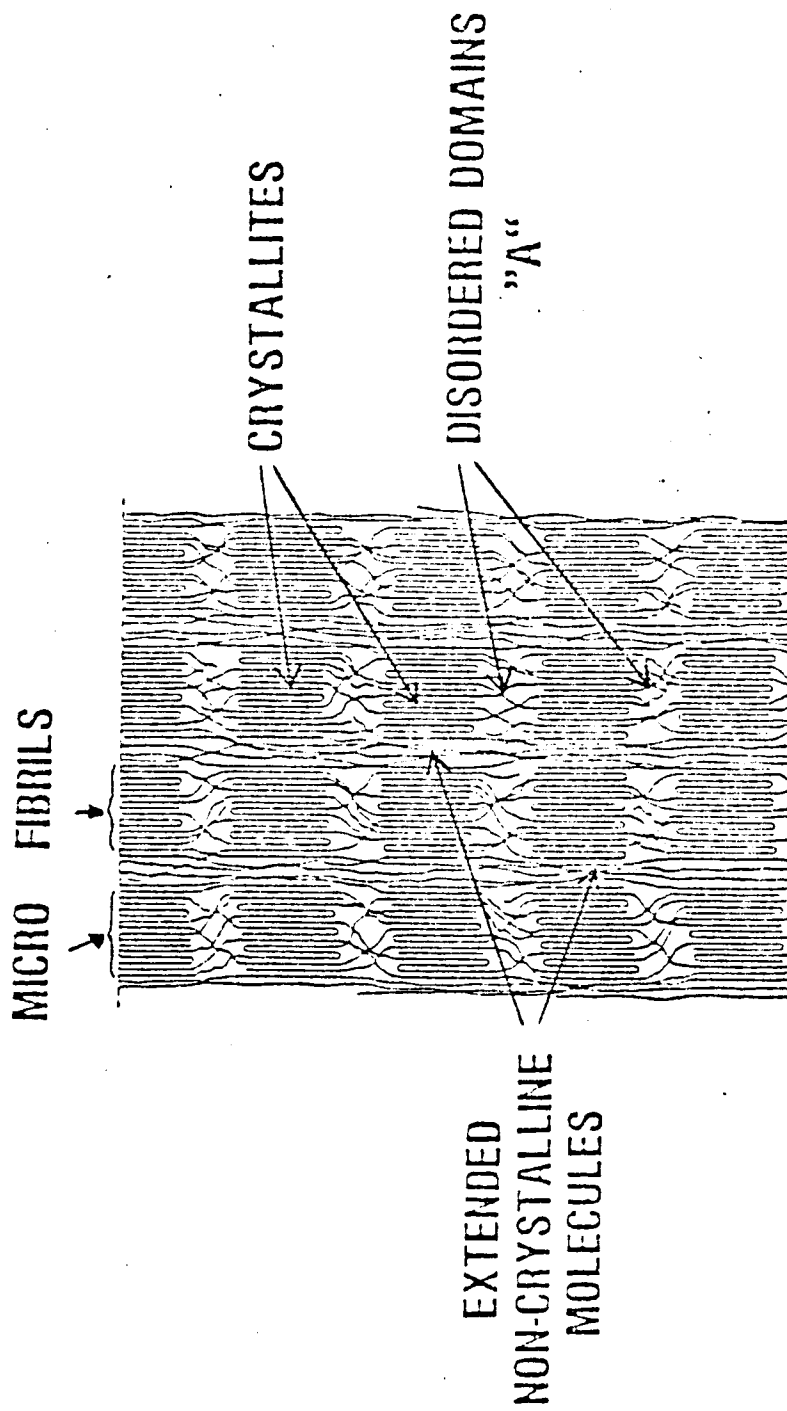
Nylon-6 fibers consist of at least three distinct phases: amorphous and crystalline domains of the microfibril and the interfibrillar matter. Almost all morphological studies of fibers show microfibrils as a well defined element structure whose width falls in the range 60-200Å. SAXS and electron microscopy has shown that microfibrils must be regarded as a separate element of fiber structure. Ironically, only

a decade ago researchers supported the idea that the fibers should be regarded as a one phase paracrystalline structure.

Several authors (26, 83) concerned with mechanical properties of fibers assume that the interfibrillar interactions are very small and thus the properties of fibers can be visualized as the properties of a loosely packed ensemble of the microfibrils. As a result, the modulus of a fiber as function of the degree of crystallinity was calculated as the modulus of an isolated microfibril. It is possible that this model is applicable to polyethylene and polypropylene fibers. With PET and nylon, the interactions between the microfibrils is sufficiently high to lead to conditions in which the crystalline dimensions have an important role in fiber strength and modulus. Hence, the microfibrillar model has to be modified.

The analysis of fiber strength is a very controversial subject. According to Peterlin (75), the fiber strength should be attributed primarily to the strength of the microfibrils while the interfibrillar domains do not contribute a great deal to fiber strength. However, Peterlin and his co-workers have worked primarily with polyethylene and polypropylene and their conclusions apply well to these two polymers. Prevorsek et al. (76, 77) believe that the extended chain interfibrillar domains are the strongest elements of fiber structure and have an important effect on fiber strength. The increase in fiber strength on drawing is attributed to an increase in the volume fraction of the extended chain molecules which are formed as a result of the relative displacement of the microfibrils. In this process the molecules from the surface of the microfibrils are sheared off and stretched. This view is rather similar to that espoused by Samuel's (84) who also

attributes increasing modulus and strength on drawing to an increase in orientation in the amorphous phase. Figure 6.9 shows a structural model for nylon-6 based on the above analysis (77).



(Fiber Axis Vertical)

Figure 6.9. Schematic Structure of Nylon-6 Fibers

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Structure Changes

Nylon-6 filaments when spun from the melt state into ambient air, do not crystallize on the running threadline but crystallize on the take up bobbin during conditioning into a partially crystalline (or paracrystalline) form with pseudohexagonal symmetry. Increasing the take up speed and SDR of the extrudate increases the density, birefringence and chain axis crystalline orientation factor as measured by WAXS. These observations suggest both increased orientation and increased crystalline fraction with increasing SDR.

In this investigation a new method of estimating the fraction of the sample which is α phase, γ phase and amorphous phase was used. This method is based on a combination of WAXS and Density data. The application of this method to the as-spun and conditioned filaments showed that filaments spun at a very low SDR have only a slight γ phase content ($X_{\gamma} < 0.1$) but do have a substantial paracrystalline α phase content ($X_{\alpha} = 0.35$). As SDR increases the α phase content decreases while the γ phase content and total crystalline content increase. At high SDR's the γ phase content levels out at about $X_{\gamma} = 0.25$ while the α phase content levels at about $X_{\alpha} = 0.2$. It is important to note that the observation of pseudohexagonal symmetry does not necessarily imply the presence of γ phase nor the absence of (paracrystalline) α phase.

When the as-spun and conditioned filaments are annealed in partial vacuum, water of a 20 percent aqueous solution of formic acid, the

pseudo-hexagonal structure (either paracrystalline α or γ) is unstable and tends to change towards the monoclinic α structure. Formic acid is most effective in this transformation, followed by water and partial vacuum. These changes cause, and are readily gaged by, increased birefringence and density of the samples. It may be noted that the chain axis crystalline orientation function is little effected by annealing. When these changes are analyzed on the basis of the new γ index, it becomes clear that both the α phase content and total crystalline content increase, the γ phase content decreases on annealing. There is also evidence that samples spun with very low SDR's anneal more readily to α phase. Those samples spun at high SDR's small amounts of γ phase even after annealing in boiling formic acid for 2 hours.

Drawing of as-spun and conditioned filaments also increases the α phase content and decreases the γ phase content. The total crystalline content increases with draw ratio for samples spun with low SDR's, but drawing has little effect on the total crystalline content of the samples spun with high SDR's. Drawing also results in substantial increases in orientation, especially for the samples spun with low SDR's.

Cold Crystallization Kinetics

The kinetics of crystallization on the bobbin after melt spinning (cold crystallization) were studied using on-line birefringence measurements on a mono-filament spinline. This approach was suitable for following the kinetics of this process provided the samples were spun at sufficiently high SDR's. Based on the accumulated evidence it appears that this process involves the formation of a paracrystalline or partially crystalline structure with pseudo-hexagonal symmetry from the oriented amorphous phase initially present after melt spinning. As described

above this pseudohexagonal structure may correspond primarily to a paracrystalline α phase at low SDR's but probably includes an appreciable γ phase content at higher SDR's. The process was found to exhibit the characteristics of a primary crystallization process followed by a secondary crystallization step. The rate of primary crystallization was greater for the higher SDR samples while the rate of the secondary crystallization process was greater for the low SDR's samples.

Mechanical Properties

Nylon-6 filaments spun at low SDR show yield points in their stress-elongation curves. Filaments spun at high SDR do not show a yield point. The tensile strength and modulus increase slowly at first, but rapidly later as a function of SDR. The elongation to break decreases with SDR. Similar trends are observed when the mechanical properties are plotted against birefringence and the c-axis crystalline orientation function.

As-spun and conditioned nylon-6 filaments when drawn at 90°C to various draw ratios show improvement in their mechanical properties. Tensile strength and modulus increase with increasing draw ratio. Elongation to break decreases as a function of draw ratio.

Recommendation For Future Research

1. Studies of drawing of nylon-6 over a broad range of temperatures are needed. The techniques developed here should be used to characterize the tendency to form α phase from the as-spun structure as a function of draw temperature and draw ratio.

2. The 0,14,0 meridional reflection should be studied in greater depth. It should be attempted to quantitatively analyze the nylon-6 filaments by use of its 0,14,0 reflections.

3. SAXS studies of the microfibrils in nylon-6 should be conducted. This would provide a correlation between the long period which represents the spacing between two adjacent crystallites and other properties.

4. A technique which computes crystallite sizes and also characterizes the degree of paracrystallinity of the various phases should be developed and used for the characterization of nylon-6 samples.

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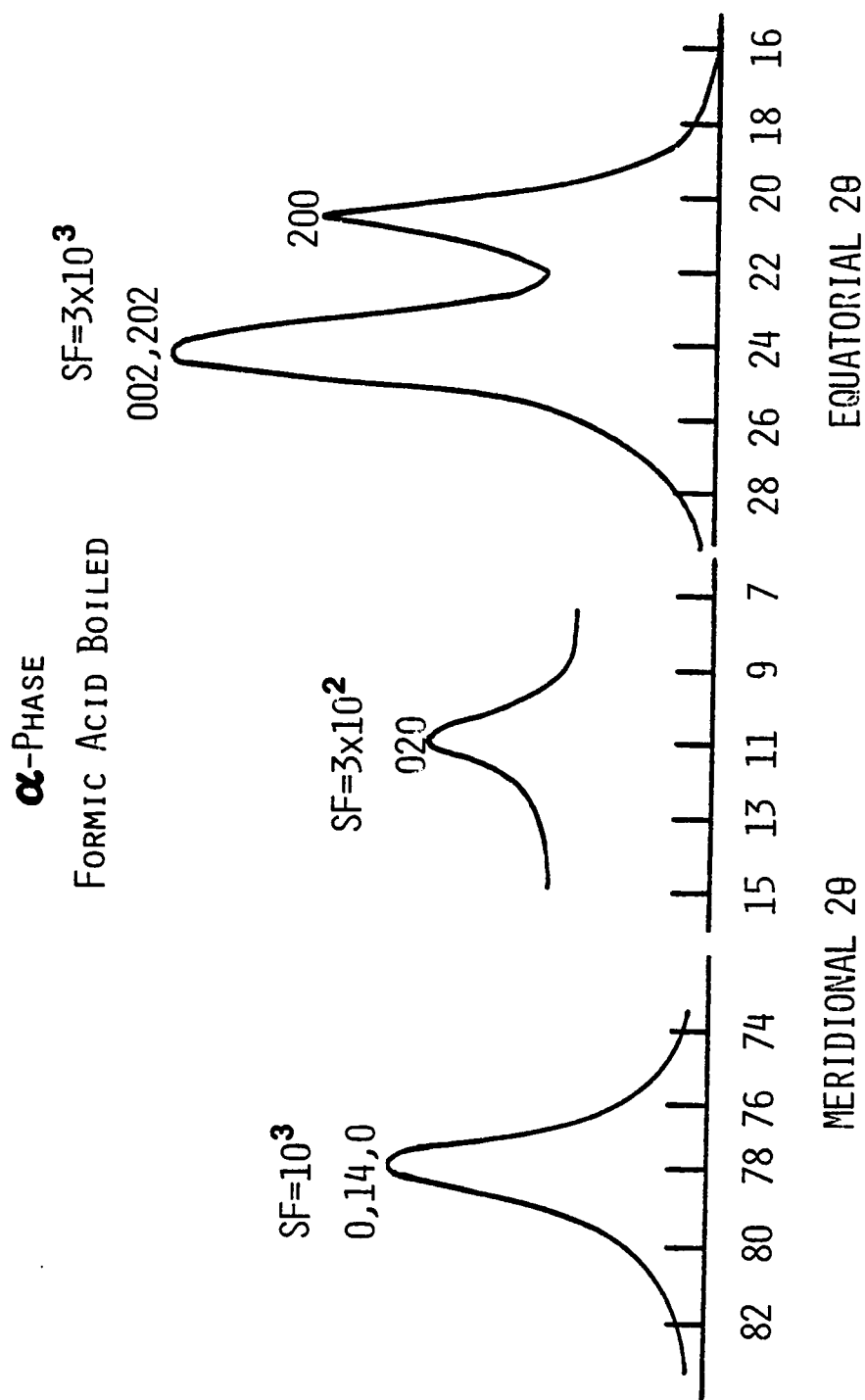
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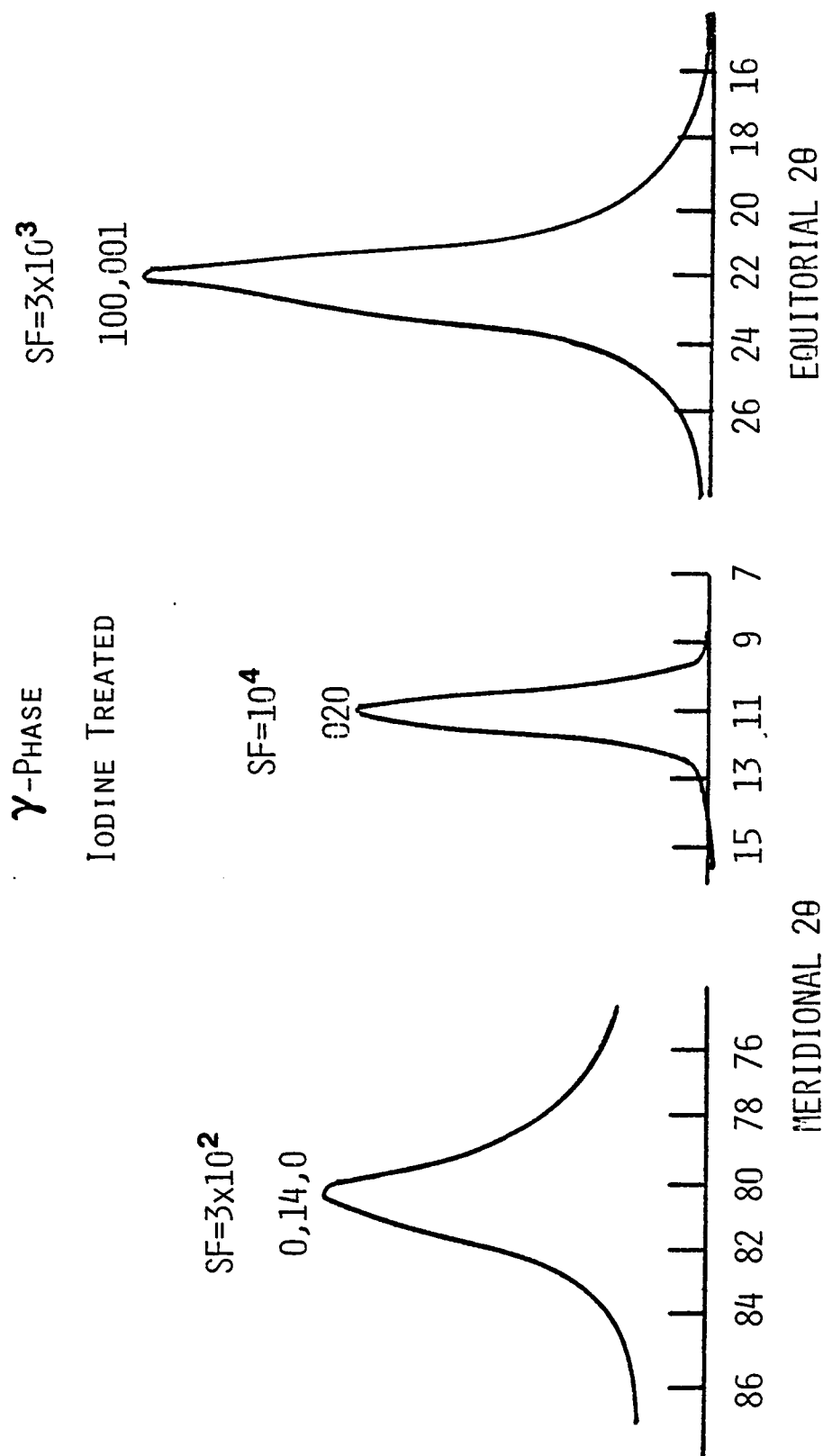
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APPENDIXES

APPENDIX A

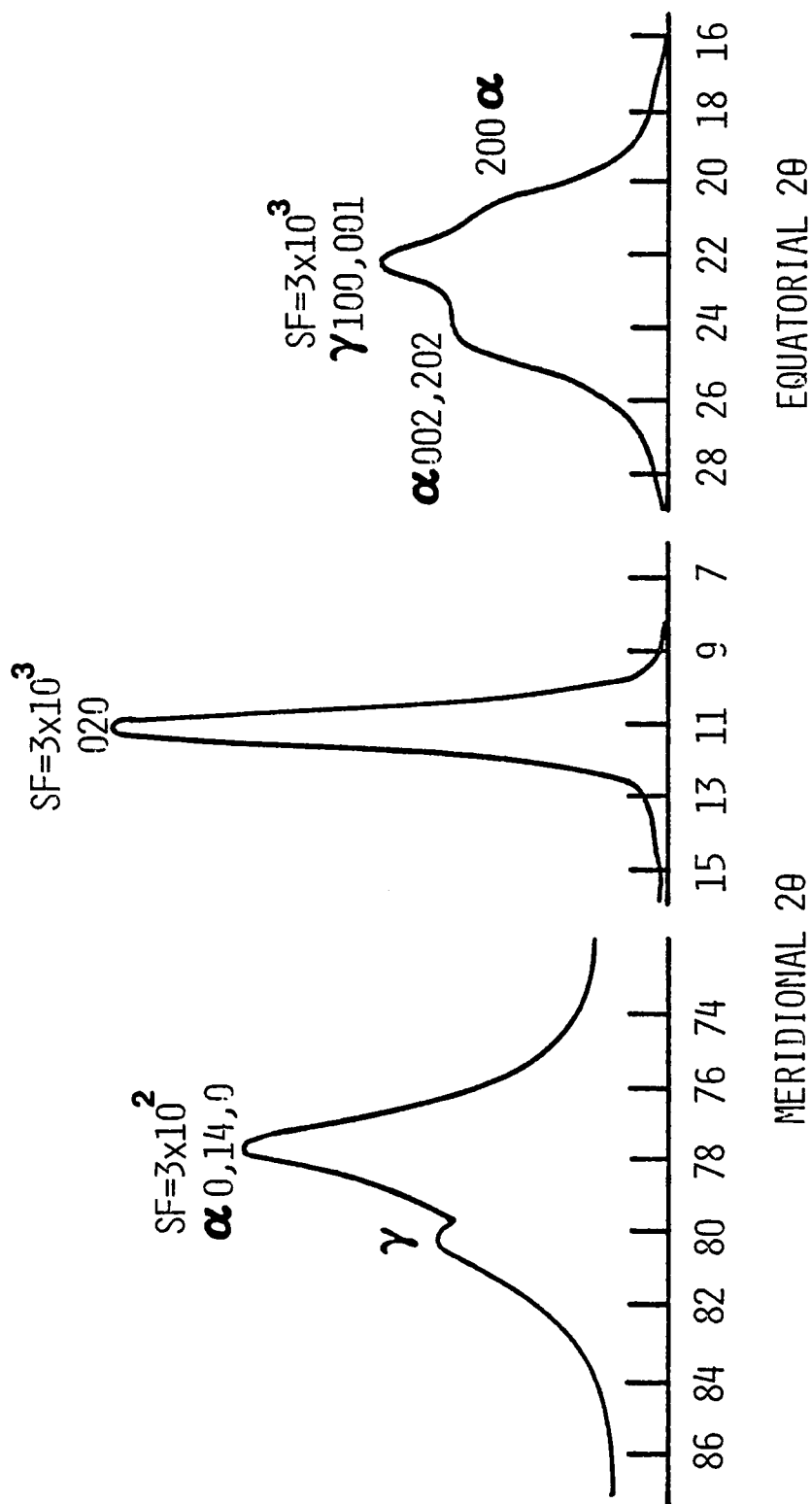


Typical WAXS Patterns for a Nylon-6 Sample High in α Content



Typical WAXS Patterns for a Nylon-6 Sample High in γ Content

PHYSICAL MIXTURE
($\alpha + \gamma$)



Typical WAXS Patterns for a Nylon-6 Sample having
a Physical Mixture of α and γ

APPENDIX B

CHARACTERIZATION OF NYLON-6 FILAMENTS BY ANALYSIS OF 0,14,0 PEAK

Results. Table VII shows the data for the characterization of nylon-6 filaments by analysis of 0,14,0 peak. The peak areas were obtained as explained in Chapter III. A γ fraction was obtained from the resolved areas.

Discussion. A more thorough analysis of the 0,14,0 peak was not undertaken due to lack of data. The one particular SDR sample analyzed shows reasonable results, Table VII. Only limited comparison can be made with the earlier results of the γ index. This is because of the inherent differences in the method for calculation of the γ fraction. The approach employed in this study assumes the 0,14,0 reflection be due to the crystalline α and γ phases only. This approach provides no correction for any disorder in the two crystalline phases. The results of Table VII are, however, very plausible.

TABLE-VII

CHARACTERIZATION OF NYLON-6 FILAMENTS BY ANALYSIS OF
OF 0,14,0 PEAK

Sample	Peak Position	$\frac{\text{Area } I_1}{\text{Area } I_1 + I_2}$
As-spun	80°	.75
As-spun, annealed in boiling water, 2 hrs.	77.93°	.52
Annealed in 20% formic acid, 2 hrs.	77.9°	.29
Drawn 2x at 90°C	79.3°	.71
Drawn 4x at 90°C	77.9°	.140
Annealed in vacuum 120°C, 2 hrs.	80°	.78
Annealed in vacuum 120°C, 3 hrs.	80°	.78
Annealed in vacuum 120°C, 4 hrs.	80°	.72
Annealed in vacuum 140°C, 1 hr. 120°C, 4 hrs.	80°	.58
Annealed in vacuum 150°C, 2 hrs.	78.4°	.63

VITA

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