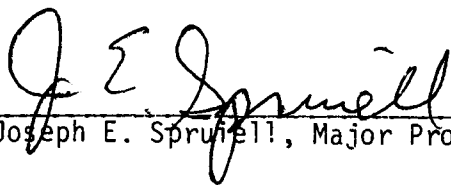
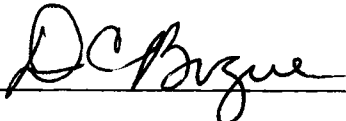


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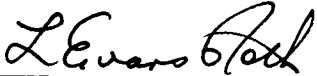
I am submitting herewith a thesis written by Galen Richeson entitled "Structure Property Relationships in Rolled Poly(ethylene terephthalate)." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


Joseph E. Spruiell, Major Professor

We have read this thesis and
recommend its acceptance:

Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

STRUCTURE PROPERTY RELATIONSHIPS IN ROLLED
POLY(ETHYLENE TEREPHTHALATE)

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Galen Richeson

August 1982

3063039

DEDICATION

This thesis is dedicated to my mother and father whose love and encouragement have made it possible for me to reach this goal.

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ABSTRACT

Poly(ethylene terephthalate) (PET) film was processed by four paths. In Path I, PET was rolled from the amorphous glassy state. In Path II, the samples were crystallized at 150°C for 12 hours and then rolled. For Path III, amorphous PET was rolled and then annealed at 150°C for two hours. In Path IV, initially amorphous films were rolled at an elevated temperature (above T_g) in an attempt to simultaneously orient and crystallize the samples. However, unsatisfactory results were obtained by Path IV so most of the research involved Paths I, II, and III.

WAXD patterns and pole figures indicate the chains in Path I samples become preferentially oriented parallel to the RD during rolling. As the chains become more oriented, the morphology changes from the initial amorphous structure to a somewhat more ordered paracrystalline structure which increases in degree of order with increases in roll reduction. Small crystallites are believed to form at the highest reductions. Density results indicate an increase in crystallinity of about 10%.

In Path II, the samples are highly crystalline and spherulitic before rolling. During rolling, the spherulites are crushed and the lamellae become tilted toward the TD. At the highest reductions, the lamellae themselves are crushed and the chains become preferentially aligned parallel to the RD. The crystallinity remains almost constant during rolling, but the density decreases.

Path III is more complicated. In this case some line nuclei are believed to form in the samples during rolling. These are a part of the strain-induced changes in structure noted for Path I samples. Upon annealing, these line nuclei give rise to cylindrites. At high reductions, these cylindrites grow in a staggered conformation which gives rise to a four-point SAXS pattern. Both the density and degree of crystallinity are relatively independent of roll reduction.

The alignment of the chains produced a significant increase in the modulus and tensile strength in the RD for Paths I, II, and III. Tensile properties in the TD were relatively unaffected by the rolling treatment. In general, Path III samples were stronger than Path II samples which were stronger than Path I samples. Path I samples were more ductile and usually had higher elongations to break than Path II or III samples.

Rolling PET by Path I and Path II allowed direct comparisons to be made between rolling of crystalline and amorphous polymers.

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CHAPTER I

INTRODUCTION

Cold rolling has been used for years as a process to reshape and strengthen metal sheeting. Cold rolling is now beginning to find acceptance in the polymer industry. The most successful application has been the production of high strength strapping used to bind large containers. Other applications include the manufacture of art tapes and ribbons, stock for deep drawn parts, and the alteration of thick sheets or films into thinner gages.

In contrast to metals, relatively little is known about the effects of rolling on polymers and many questions remain largely unanswered. For example, rolling is known to increase the tensile strength of most polymers in the roll direction, but what is the morphology responsible for the increase and by what mechanism is this morphology produced? How anisotropic are properties of rolled sheets? For example, how is the tensile strength in the transverse direction related to the tensile strength in the roll direction and how is this explained by the morphology? Is it possible to predict mechanical or physical properties knowing the morphology? What degree of rolling is necessary to produce the optimum properties? Obviously, much research is needed to better understand the changes which take place in polymers during rolling and the mechanism by which they occur.

Most of the work in the literature on rolling of polymers is concerned only with the changes in mechanical properties and very little consideration is given to the morphology. There are, however, two

important works in which an attempt is made to determine the morphology formed by rolling and the mechanism by which it is formed. The first is Gezovich and Geil (28) working with polyoxymethylene and the second is Dhingra (16) working with polypropylene. Both of these polymers are highly crystalline and have a simple chemical repeat unit.

Poly(ethylene terephthalate) (PET) was chosen to be studied in the present research on rolling for two main reasons. The first is for practical considerations. PET is an important commercial polymer used in both fiber and film applications as a result of its good mechanical and physical properties. Thus, research on this polymer would be of interest to many people. Because of its wide applications there has been much work reported in literature on the drawing of PET fibers and films. This existing knowledge provides a basis for the understanding of the mechanical and morphological changes which take place during rolling. Rolling is similar to drawing in the sense that due to friction the rolls exert a force on the polymer which has a tensile component in the roll direction but is different in that a compressive force is exerted in the thickness direction.

The second reason for choosing PET was because its complex chemical structure and semi-crystalline nature make it significantly different from the polymers in previous investigations of the morphology produced by rolling. In contrast to either non-crystallizable polymers or polymers which crystallize quite rapidly from the melt, the sluggish crystallization kinetics of PET allow the study of both amorphous and crystalline forms of this polymer. In this way a direct comparison of the effects of rolling can be made between crystalline and amorphous

polymers without having to take into account the differences between the polymers themselves.

Several different processing paths were chosen to take advantage of the slow crystallization kinetics of PET. Both amorphous and crystalline forms were rolled. Another path involved annealing rolled amorphous samples. In a fourth path an attempt was made to roll and crystallize the polymer simultaneously.

Rolling was followed by a thorough investigation of the morphology and mechanical properties. In this way a better understanding can be obtained of the relationship of mechanical properties to the morphology and of the mechanism by which these morphologies are produced during rolling. The changes that occur in the amorphous form can be compared to those that occur in the crystalline form and some of the basic differences produced by rolling can be defined and perhaps explained in terms of the morphology.

CHAPTER II

LITERATURE SURVEY

A. STRUCTURE AND PROPERTIES OF PET

Basic Physical and Chemical Properties

The chemical formula for PET is $-(\text{CO} - \text{C}_6\text{H}_4 - \text{CO} - \text{O} - (\text{CH}_2)_2 - \text{O})_n-$. The formula molecular weights are typically low compared to addition reaction polymers such as polyethylene or polypropylene. Heffelfinger reports a number average molecular weight $\bar{M}_n$ of about 15,000 and an intrinsic viscosity (IV) of about 0.54 to 0.56 (32). PET can, however, be obtained with a $\bar{M}_n$ as high as 40,000 and intrinsic viscosities greater than 1.0 (53).

PET is formed by a condensation reaction of terephthalic acid or dimethyl terephthalate with ethylene glycol. Since water (or methanol) is given off in the reaction, molten PET must not come in contact with water, acids, or halogens since these can cause depolymerization reactions. The rate of hydrolytic degradation can be very high in the melt even if only a small amount of water is present. In the solid form PET is less susceptible to degradation (50). In one study, PET was shown to have no appreciable loss of strength after soaking in water at 70°C. At 100°C the tensile strength was reduced by 60% after three weeks of immersion. At 150°C in moist air, the loss of strength was 25% after six weeks. Virtually all the degradation was attributed to hydrolysis (50). So it appears that heated at low temperatures and low humidity for relatively short periods of time there will be no appreciable degradation in PET.

Solid PET absorbs very little water compared to other polymers. At 65% relative humidity and 20°C, the moisture regain is only 0.4%. At 100% relative humidity the absorption is 1% (50). The maximum recommended moisture content prior to melt fabrication, however, is 0.005 wt.-% (1). Hence, PET must be rigorously dried before melt processing.

Due to its sluggish crystallization kinetics, PET can exist in either an amorphous or crystalline form. If the polymer is quenched from the melt quite rapidly, it will be amorphous. If it is allowed to cool slowly it will crystallize.

Amorphous PET can be crystallized at temperatures higher than its glass transition temperature T_g , but lower than its crystalline melting point T_m . Under quiescent conditions PET crystallizes very slowly except in the range of about 120°C to 220°C. The maximum rate of crystallization is between 155°C and 190°C (1, 5, 37, 71).

The melting point for commercial grade PET is typically about 255°C while highly crystalline samples will melt at temperatures as high as 270°C (1). The relatively high melting point of PET is probably due to the rigidity of the aromatic ring and the attached -CO-O- groups (14).

In amorphous samples, the glass transition temperature occurs at about 70°C (1).

The density of PET ranges from 1.333 at room temperature for the amorphous state to 1.41 g/cm³ for a highly crystalline sample (14, 32).

The density can be easily measured by means of a density gradient column. Mixtures of n-heptane and carbon tetrachloride as well as

sodium bromide and water have been used successfully (6, 52, 71). Statton observed excessively high density values (as compared to x-ray crystallinity) in his strained samples which he attributes to a preordering process which increases the effective density of the amorphous phase (73). Yeh reports that PET shows a significant improvement in atomic packing upon stretching in the glassy state (88). Hence, care must be taken in interpreting density increases as increases in crystallinity.

Pure amorphous PET is colorless. It becomes opaque (almost white) due to the addition of TiO_2 , a delustrant, or upon crystallization if the spherulites are large. The appearance can range from lustrous and semitransparent to dull white and opaque depending on the percentage of delustrant or crystallinity (58).

PET has good chemical resistance. Long exposure to weak or moderately strong solutions of inorganic alkalis, acids, and salts at room temperature cause little or no shrinkage and have only small effects on the strength. Exposure at high temperatures causes some loss of tensile strength. Organic substances in general have little chemical effect on PET (54). They may, however, cause swelling. Swelling agents may reduce Young's modulus, the yield stress, and the fracture stress while increasing the elongation to break (45).

In order to determine the IV, a good solvent must be found. PET is soluble in various mixtures of phenol and tetrachloroethane (32, 52, 54, 55). Other solvents are "ortho"-chlorophenol, dichloroacetic acid, trifluoroacetic acid, "meta"-cresol and a mixture of trichlorophenol and phenol (54, 55).

PET shows linear and time dependent elastic behavior. The viscoelastic behavior involves two mechanisms. In one mechanism polymer chains slide by each other by the relative movement of their centers of gravity (viscous behavior). In the other, polymer chains tend to uncoil or extend in the direction of the tension (elastic behavior).

Mechanical properties of interest include elastic modulus, yield strength, tensile strength, and elongation to break. Typical values for unfilled polyester sheets follow (50).

	<u>Unoriented PET</u>	<u>Oriented PET</u>
Tensile Strength (1)	8,000 psi	25,000 to 36,000 psi
Young's Modulus (34)	400,000 to 600,000 psi	1,750,000 psi
Elongation to Break (73)	50% to 300%	12% to 130%

The tensile strength and initial elastic modulus of PET fibers have been shown to increase with increasing molecular weight (50).

Fiber samples were reported to show good dimensional recovery from stretching, bending, and shearing. Samples that were loaded rapidly and released immediately showed the following recovery after one minute.

<u>% Stretch</u>	<u>% Recovery</u>
2	97
4	90
8	80

Table 2A-1 shows results obtained for slow rates of loading (58).

TABLE 2A-1
PERCENT RECOVERY FOR SLOW RATES OF LOADING

% Stretch	Low Elongation Yarn (70°F)		High Elongation Yarn (70°F)
	% Recovery (dry)	% Recovery (wet)	% Recovery
0.5	92	92	97
1.0	71	79	85
2.0	60	60	54
5.0	64	-	32

Source: J. Press, "Man-Made Textile Encyclopedia," Textile Book, London, 117, 1959.

Crystal Structure

The unit cell of PET was determined by Daubeny, Bunn, and Brown (14). It is triclinic and contains one chemical repeat unit (see Figure 2A-1). The following lattice parameters were reported.

$$\begin{array}{lll} a = 4.56 \text{ \AA} & b = 5.94 \text{ \AA} & c = 10.75 \text{ \AA} \\ \alpha = 98.5^\circ & \beta = 118^\circ & \gamma = 112^\circ \end{array}$$

The theoretical density for the crystal then is 1.455 g/cm^3 . The highest density found for highly drawn yarn is, however, only about 1.41 due to the incomplete and imperfect crystallization of PET. The density of amorphous PET can be measured directly since entirely amorphous PET is available. Daubeny et al. reported the amorphous density as 1.335. Mehta et al. adopted the value of 1.336 (52), while Heffelfinger and Burton used 1.333 (32).

The crystalline density as reported by Bunn et al. may be too low. Values of 1.495 (41) and 1.501 (94) were reported several years later by others. These values were obtained by remeasuring the crystal plane spacings $d_{(100)}$ and $d_{(010)}$ while using Bunn's values for the other unit cell parameters (25).

Fakirov, Fischer, and Schmidt (25) recently redetermined the unit cell and reported slightly different values than Bunn.

$$\begin{array}{lll} a = 4.48 \text{ \AA} & b = 5.85 \text{ \AA} & c = 10.75 \text{ \AA} \\ \alpha = 99.5^\circ & \beta = 118.4^\circ & \gamma = 111.2^\circ \end{array}$$

The crystalline density for this unit cell is 1.515 g/cm^3 .

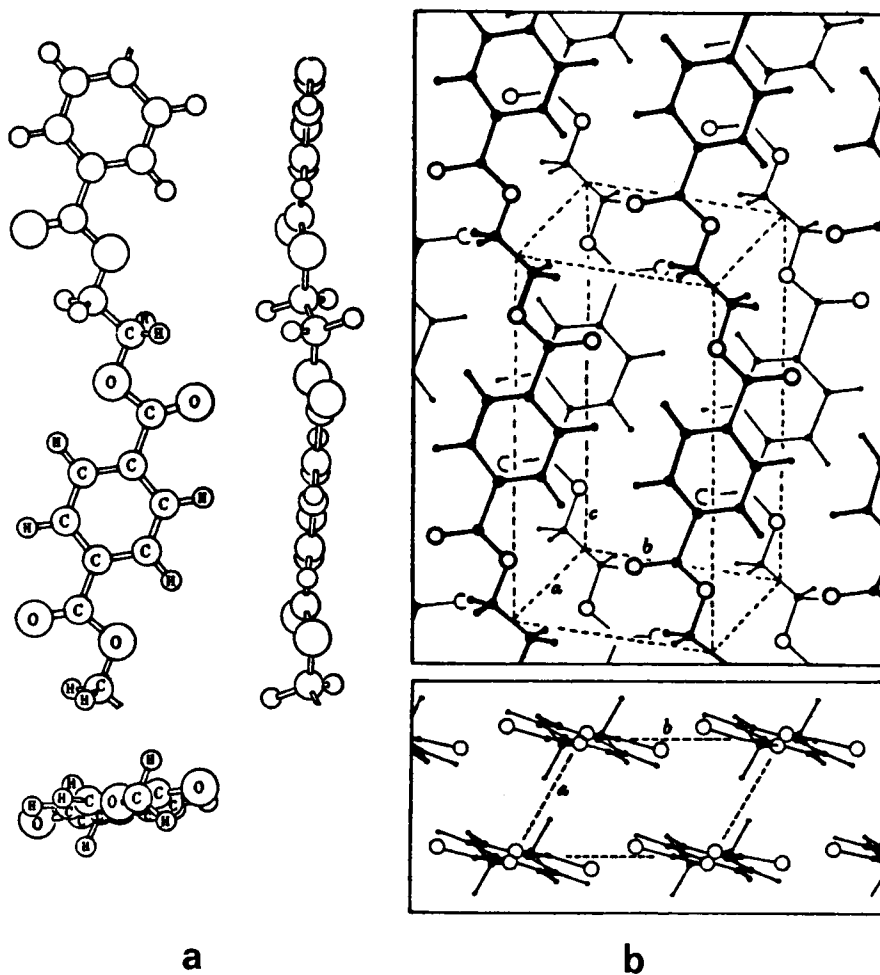


Figure 2A-1. (a) Conformation of PET molecule. (b) Arrangement of the chains in the triclinic unit cell.

Source: R. Daubeny, C. Bunn, and C. Brown, Proc. Roy. Soc. London, A226, 531-542 (1954).

This value is important in determining the percent crystallinity by the density method.

The fiber repeat distance of $10.75 \text{ \AA}$ is consistent with the theoretical value of $10.9 \text{ \AA}$ for a fully extended planar chain. The packing of the chains seems to be primarily dependent on their shape. The molecules are nearly planar with the carbon and oxygen atoms just out of the plane of the benzene ring. The $-\text{CO}-\text{O}-$ group is tilted about 12° out of the plane of the benzene ring and the glycol group is tilted about 20° (14). The configuration of the molecules and their arrangement in the unit cell are illustrated in Figure 2A-1.

Crystallization of PET

By rapidly quenching extruded PET films, completely amorphous samples can be obtained. Crystallization can be brought about by annealing the polymer at a temperature between T_g and T_m or by stretching the polymer. The latter is known as "strain induced crystallization."

Crystallization is of commercial significance because of the stability it imparts to the oriented polymer.

1. Kinetics and Morphology of Quiescent Crystallization

Thermally induced crystallization is dependent on the temperature, the length of time of the heat treatment, previous thermal history, and molecular orientation. The latter effect will be discussed in a separate section.

For unoriented quiescent samples, the temperature determines the rate of crystallization. The half times of crystallization as a

function of temperature have been determined by Cobbs and Burton (13) and by Mayhan, James, and Bosch (51) among others. Crystallization occurs very slowly below about 100°C and above about 250°C. Crystallization occurs relatively fast between about 140 to 220°C with the maximum rate being around 180 to 190°C.

Spruiell, McCord, and Beuerlein (71) also found the crystallization rate to be highest at about 190°C. At 190°C the half time of crystallization is about one minute whereas at 130°C it rises to six minutes. To obtain the maximum crystallinity at a given temperature the samples were annealed for a period of time equal to ten times the half time of crystallization at that temperature. The maximum final level of crystallinity was shown to increase with increasing temperature.

Mayhan, James, and Bosch have studied the crystallization kinetics of unstrained PET using light transmission techniques (51). They reported no detectable crystallization until the glass transition temperature was exceeded by 30°C. They also measured maximum density as a function of temperature and observed four regions of behavior. No crystallization was detected in the transition zone (70 - 95°C), but the authors surmised that there was probably sufficient thermal motion of the chain segments for primary nucleation sites to form. It is also possible that some nucleation sites could have formed during the initial quenching.

Above the transition zone, there were three crystallization zones. The crystallization in Zone I (95 - 110°C) was believed to occur as a result of initial nucleation. In Zone II (110 - 200°C),

the increase in crystallinity was less than in Zone I. This suggested that crystallization occurred by growth of existing crystallites. Also, it was suggested that low molecular weight fractions of the polymer were pushed aside by the growing spherulites in Zone I. As the crystallization process continued the low molecular weight fractions must have become trapped in pockets between the initial crystalline regions slowing the spherulite growth. Above 200°C (zone III), the increase in crystallinity was attributed to secondary crystallization. This involved the previously uncrystallized low molecular weight material trapped in pockets and other areas where the chains had restricted movement.

The initial crystallization kinetics were modeled as a first order kinetic process. The differential equation governing this process was given by

$$-\frac{dx}{dt} = k_1 (a - x)$$

where "x" is the amount of crystalline polymer formed, "a" is the amount of amorphous polymer available, "t" is time. and "k₁" is the rate constant. The rate constants were then calculated from the half times of crystallization. Table 2A-2 shows their results.

From a plot of the inverse of the rate constant as a function of the inverse temperature the apparent activation energy was calculated to be 37 kcal/mole of segment crystallized.

The Avrami equation which describes crystallization kinetics may be written as follows for polymers:

$$v_x = z (1 - e^{bt^n}) \quad 1 < n < 4$$

TABLE 2A-2
CRYSTALLIZATION RATES AS A FUNCTION OF TEMPERATURE

Crystallization Temperature, °C	Half Life, min.	Rate Constant $k_1 \times 10^3, \text{min.}^{-1}$
96.5	84	8
100.0	64	11
102.5	43	16
110.0	14.5	48
112.5	9.5	73
119.5	3.5	198
132.0	1.0	Not Determined

Source: K. G. Mayhan, W. J. James, and W. Boxch, J. Appl. Poly. Sci., 9, 3605-3616 (1965).

where v_x is the volume fraction of crystalline polymer, and z is the limiting fraction of crystalline polymer at a specific temperature.

"b" contains information on the nucleation rate and growth constants, and "n" varies from 1 to 4 depending on the geometry of the nucleation and growth.

Values of "n" were found to lie between 1 and 2. Mayhan et al. (51) conclude that the growth in the initial stages of crystallization is one dimensional. Cobbs and Burton (13) suggest that from 120⁰ to 240⁰C, platelike growth is favored.

Keller (39), Zachmann and Stuart (93), and Yeh and Geil (90) have all reported spherulitic growth in unoriented PET crystallized from the glassy state.

Keller found that when the spherulites were separate, as in partially crystallized material, they were spherical in shape. When they were in close contact they became polyhedral in shape. Crystallization nucleated from lines and surfaces produced other shapes.

Yeh et al. investigated the temperature at which crystallization could be first observed. He reports the morphology of glassy, amorphous PET is characterized by "ball-like structures in which a paracrystalline type order is present." At annealing temperatures near T_g , the balls began to aggregate and align. At 60⁰C, incipient spherulitic structures were observed. At 66⁰C, the structures became much larger and spherulitic fibrils could be seen. Upon annealing at 154⁰C, well defined three-dimensional spherulites were observed.

2. Strain Induced Crystallization and Resulting Morphology

Strain Induced Crystallization. Strain induced crystallization in initially amorphous PET has been studied by A. B. Thompson (77), Spruiell, McCord, and Beuerlein (71), Smith and Steward (69), Yeh (88), Stein (75), and others. All investigators found that any external stress increased the rate of crystallization many times at a given temperature.

Thompson found that the maximum rate of crystallization under zero stress, measured as a density change, is about 10^{-2} gm/cm³/sec giving rise to spherulites, but when samples have been highly drawn the rate rises to 10 gm/cm³/sec giving rise to oriented fibrils with a crystallite size 1000 times smaller. This suggested that stress greatly increased nucleation rates, making the original number of nucleation sites existing under zero stress negligible. Thus the normally slow spherulite growth process had no time to occur under high stress.

The theory Thompson developed suggests that all crystallization is strain induced. At one extreme the growth is slow and spherulitic and depends on the residual thermally induced strains, while at the other extreme growth is fast and fibrillar and dependent on the externally applied strain.

Smith and Steward (69) have studied the effects of orientation on the crystallization of initially amorphous PET samples. They found that even small amounts of orientation produced a large effect on the rate of crystallization. Greater orientations further reduced the half-time for crystallization. Increased molecular weight reduced the rate of crystallization. Nucleation and the initial growth of crystallites in

oriented PET required on the order of a few milliseconds as opposed to minutes in unoriented samples. The main effect of orientation, therefore, is to reduce the nucleation time or induction period. Mechanical orientation assists nucleation by bringing chain segments into more favorable positions for crystallization, thus reducing the conformational entropy change needed.

Smith and Steward point out that strain itself does not produce crystallization as implied by the term "strain induced crystallization." It is molecular orientation brought about by the strain that may increase the rate of crystallization. Relaxation effects may reduce the molecular orientation and hence the rate of crystallization. This implies that "stress induced crystallization" may be a more appropriate name.

Spruiell, McCord, and Beuerlein experimented with various PET samples strained at 0°, 24°, 60°, 80°, and 100°C and subsequently annealed at 80°, 96°, 105°, 190°, or 215°C. Samples strained at 0°C broke in a brittle manner so no further work was performed on these samples. No significant difference was found between the as-strained crystallinity of samples strained at 24°C and 60°C. The crystallinity increased with strain rate from about 22% at a strain rate of 0.04 min⁻¹ to about 28% at 2.0 min⁻¹.

Upon straining PET above T_g , two deformation regimes were observed. At low deformation rates, viscous flow was observed, necking did not occur and little or no crystallinity was produced. At higher deformation rates, a high degree of chain orientation was produced and necking with crystallization was observed.

Resulting Morphology. Yeh (88) concluded that, in general, strain induced crystallization tended to result in a fibrillar morphology, a high degree of c-axis orientation, and a melting point elevation. The fibrils tended to be limited in diameter to about $100 \text{ \AA}$ and to about $50 - 100 \text{ \AA}$ for PET in the stretch direction. Yeh suggested that the fibrils provided a backbone on which the lamellar crystals could grow.

Stein (75) used light scattering to analyze the morphology of the crystalline superstructure of PET strained at 80°C . His observations indicated that stress induced crystallization in PET occurred in a slightly different manner from the generally accepted "shish-kebab" mechanism of other polymers.

At low extensions (about 40%), the patterns were characteristic of the scattering of rod-like structures oriented perpendicular to the stretch direction. With increasing extension, less pronounced perpendicular orientation was indicated and the patterns became more characteristic of spherulite-like structures. At 175% elongation, the patterns indicated the spherulites were becoming elongated in a direction perpendicular to the stretch direction.

The absence of horizontal streaks in the patterns indicated that the crystallites did not grow from fibrils oriented parallel to the stretch direction, but rather from structures oriented perpendicular to the stretch direction which may have been "single crystal-like precursors of spherulites."

3. Thermally Induced Crystallization of Oriented PET and Resulting Morphology

Spruiell et al. (71) have studied the crystallization kinetics of PET samples crystallized under different conditions. They found the crystallization rate depends on the temperature and sample orientation. The strained samples crystallized many times faster and reached a higher ultimate level of crystallinity at a given temperature than did similar unstrained samples. They attributed this behavior to the "growth of or nucleation on the crystallites induced by the deformation and remaining after the very rapid stress relaxation." They found that the crystallite size increased with either the deformation or annealing temperature. Increasing the deformation temperature, however, increased the mobility of chain segments so that higher strain rates were needed to generate the critical stress level within the material that was needed to bring the chains into a position favorable for crystallization.

Koenig and Hannon (46) showed that according to an infrared analysis, no regular chain folding occurred in strain crystallized samples, but that regular chain folding occurred after annealing. They presented a possible conformation for the regular fold in annealed PET (see Figure 2A-2) (45).

Spruiell et al. (71) theorized that few folds were present in the as-strained PET samples, but upon annealing, the molecules first rapidly rearranged to relieve the internal stress and then recrystallized in a folded chain morphology. The recrystallization was probably nucleated on remaining crystalline or paracrystalline regions.

Yeh proposed a "fibrillar-to-lamellar" transformation during

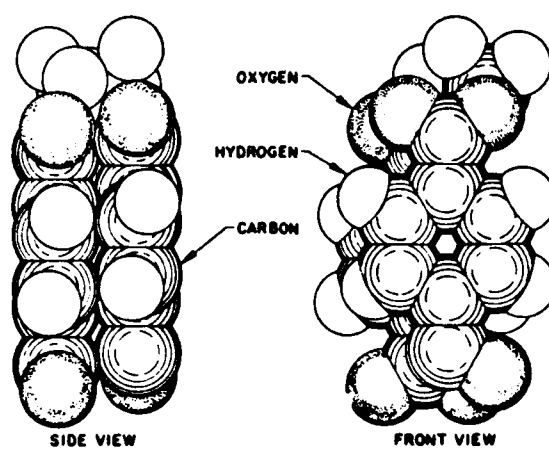


Figure 2A-2. Diagram showing a possible conformation of the fold in a PET chain.

Source: J. L. Koenig and M. J. Hannon, J. Macromol. Sci. - Phys., B1, 119 (1967).

annealing (89). The driving force is the reduction of total surface free energy by means of the lateral alignment of the smectic crystallites produced during strain induced crystallization. The transformation is limited by the tie molecules between crystallites, so that the extent of lamellar formation is affected by applied strains during annealing, degree of crystallinity, and possible molecular weight.

Yeh noted that for PET strained 100%, the fibrillar-to-lamellar transformation seemed complete, while in samples stretched 600% the fibrillar morphology seemed almost intact. Presumably, the higher level of crystallinity and rigidity of the highly drawn sample prevented the transformation from occurring.

Yeh and Geil (90, 91) proposed a ball-like structure for amorphous PET. The spheres were $75 \text{ \AA}$ in diameter and seemed to have a paracrystalline-like order. The alignment of adjacent chains was aided by the planarity of the chemical repeat unit. Numerous tie molecules connected the spheres. Upon annealing, lamellae were believed to be initially formed by the alignment and rotation of adjacent balls.

The long period as determined from small angle x-ray scattering (SAXS) was found to increase with annealing temperature. This is in good agreement for other polymers crystallized from the melt. But, the long period decreased with time at a given temperature, which is the opposite of what is found for other polymers crystallized from the melt. The heat treatment allowed the highly irregular existing chain folds to become more regular. This reduced the maximum fold period and allowed closer packing of the lamellae. Hence, the observed reduction in long period was seen. The long period of $147 \text{ \AA}$ after annealing at 200°C agreed well

with the center to center distance of $150 \text{ \AA}$ measured between spheres on the electron micrograph.

The four-point SAXS pattern observed for samples stretched and subsequently annealed at 180°C was believed to originate from inclined rows of balls which were seen in the electron microscope. The two point pattern was attributed to rows of balls aligned more or less perpendicular to the stretch direction.

Klement and Geil (42) observed much the same thing as Yeh and Geil (83, 84). Uniaxially drawn thin films ($1700 \text{ \AA}$) were reported to have $100 \text{ \AA}$ nodules which aligned in short rows aligned at about 40° to the stretch direction. Annealing the oriented structure caused the rows to rotate so that at the highest annealing temperature they were oriented nearly perpendicular to the stretch direction. Uniaxial drawing caused the nodules to rotate so that the chain axes paralleled the draw axis.

Bright field microscopy showed evidence for the existence of $200 - 500 \text{ \AA}$ morphological units which they term supernodules. Baker (4) also reported $500 \text{ \AA}$ spheres, after etching with n-propylamine. These structures were believed to be groups of nodules interlinked by a higher than average number of the molecules. The supernodules tended to move as a unit during deformation. More of the deformation occurred between the supernodules than between nodules, possibly because of the greater number of tie molecules within the supernodule. A model describing the morphology of undrawn and drawn PET was proposed (see Figure 2A-3).

After annealing, the oriented PET was found to consist of small

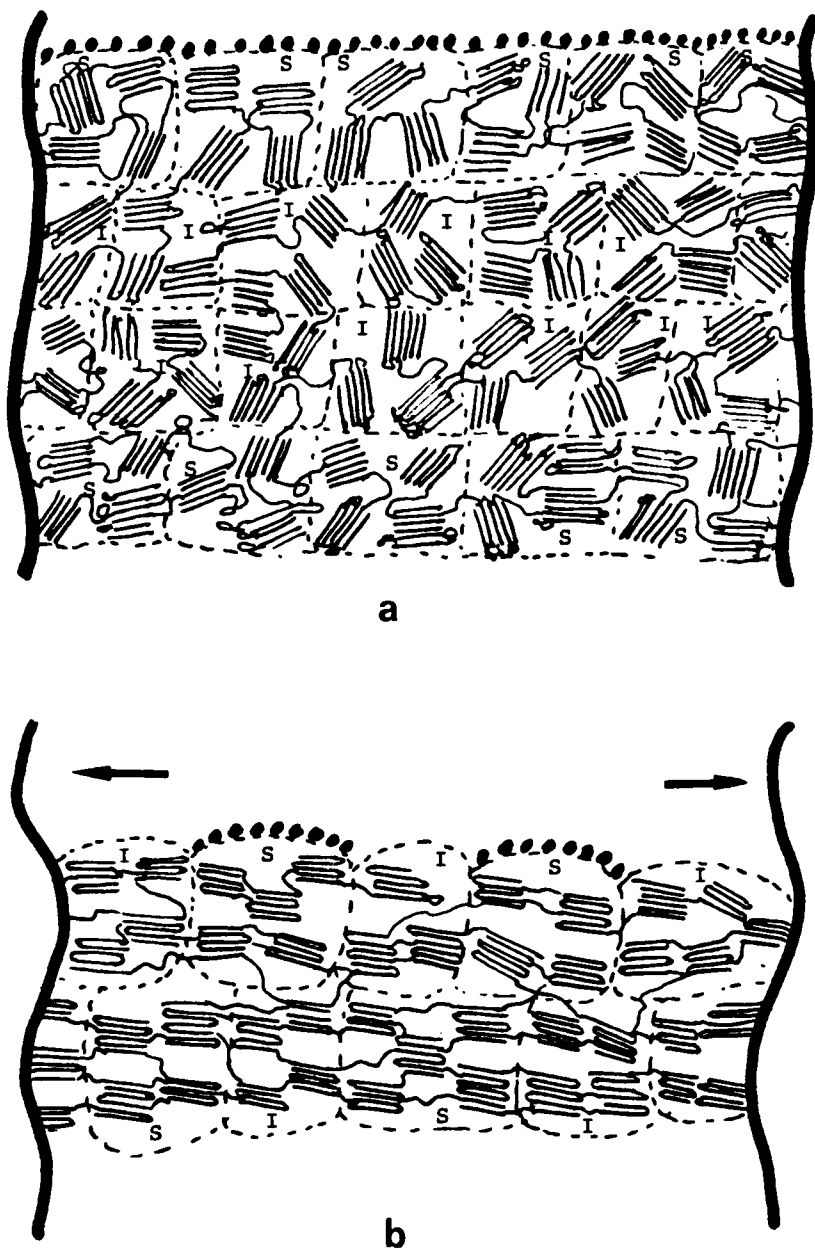


Figure 2A-3. (a) Schematic model showing the arrangement of nodules (regions with aligned chains) and supernodules (dotted lines) in undrawn PET. Surface nodules are labeled "S" and interior nodules are labeled "I." (b) Same film after drawing and annealing. Note that some interior nodules have moved to the surface.

Source: J. J. Klement and P. Geil, J. Macromol. Sci. - Phys., B5, 535-558 (1971).

(140 $\text{\AA}$)⁰ crystallites. During stretching and annealing, these crystallites were able to move about. In biaxially stretched films, the (100) planes were found to lie preferentially within the plane of the film. It could not be determined whether the alignment occurred during stretching or annealing.

The existence of the nodules and the small crystallites was believed to increase the ductility of the polymer by providing a stress relaxation mechanism. The mechanism was the relative movement of the nodules.

Klement and Geil (43) also studied thick (5 - 30 mil) films. Ten mil samples were uniaxially drawn 4X at 90°C. After annealing at 240°C for 15 minutes, a definite pattern of striations were seen in electron micrographs running generally perpendicular to the stretch direction. The striations were proposed to be either lamellae stacked edgewise to the plane of the film or fibrillar structures having two small and one large dimension. The center-to-center distance between lamellae was reported as 200 $\text{\AA}$ ⁰. The fibrillar lamellar structure did not appear in samples annealed at less than 180°C. Samples annealed at 120°C and 150°C showed only the 200 - 400 $\text{\AA}$ ⁰ nodules. Surface undulations (2000 - 5000 $\text{\AA}$ ⁰) were believed to be caused by the relaxation of the polymer during annealing.

Uniaxially drawn and annealed samples showed a slight tendency for the (100) plane to lie in the plane of the film. Otherwise, the WAXD patterns were similar to PET fiber patterns.

At high annealing temperatures (>240°C) the structure in both

uniaxially and biaxially stretched films tended to be fibrillar. In uniaxial samples the fibrils were oriented preferentially perpendicular to the stretch direction, which was consistent with their results for PC, i-PMMA, i-PS, and thin films of PET. The transition from nodular to fibrillar structures occurred at 180°C which is where the maximum rate of crystallization occurs for PET. The nucleation-controlled crystallization (as opposed to transport-controlled crystallization at lower temperatures) could have been responsible for the larger morphological units.

No discrete small angle scattering was observed for any of the drawn films before annealing, although uniaxial drawing temperatures ranged from 45 to 110°C . Discrete scattering was observed after annealing in the range of 120 to 240°C . Small angle spacings were $77 - 100 \text{ \AA}$ after annealing at 180°C and were $100 - 142 \text{ \AA}$ at 240°C .

After annealing at 180°C and 240°C the uniaxial samples showed a four-point SAXS pattern in both the "edge" and "through" positions.

Both small angle flat-plate photographs and a series of small angle pole figures at different Bragg angles were made. Based on these results, the authors envisioned the region of maximum pole density for four-point scattering to be a flattened toroid in reciprocal space (see Figure 2A-4).

The authors proposed a model for the structure in real space responsible for the four-point patterns (see Figure 2A-5):

The essential ingredient is a structural segment of fixed length and orientation as indicated by c in Figure 2A-5a. Lateral alignment of these segments will define the surfaces of a layer. A regular vertical shift of each segment will produce surfaces at varying angles to c and with varying

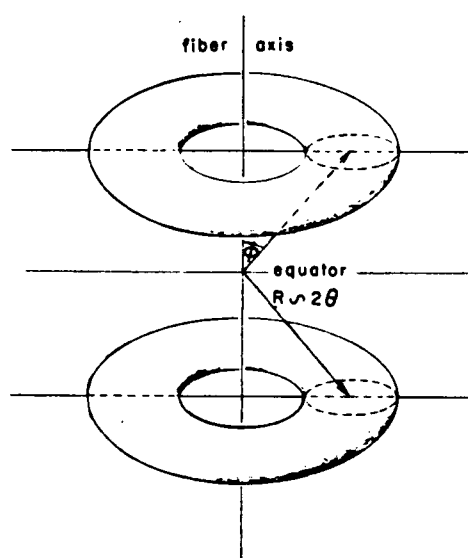


Figure 2A-4. Three dimensional representation of the SAXS pattern in reciprocal space.

Source: J. J. Klement and P. Geil, J. Macromol. Sci. - Phys., B5, 535-558 (1971).

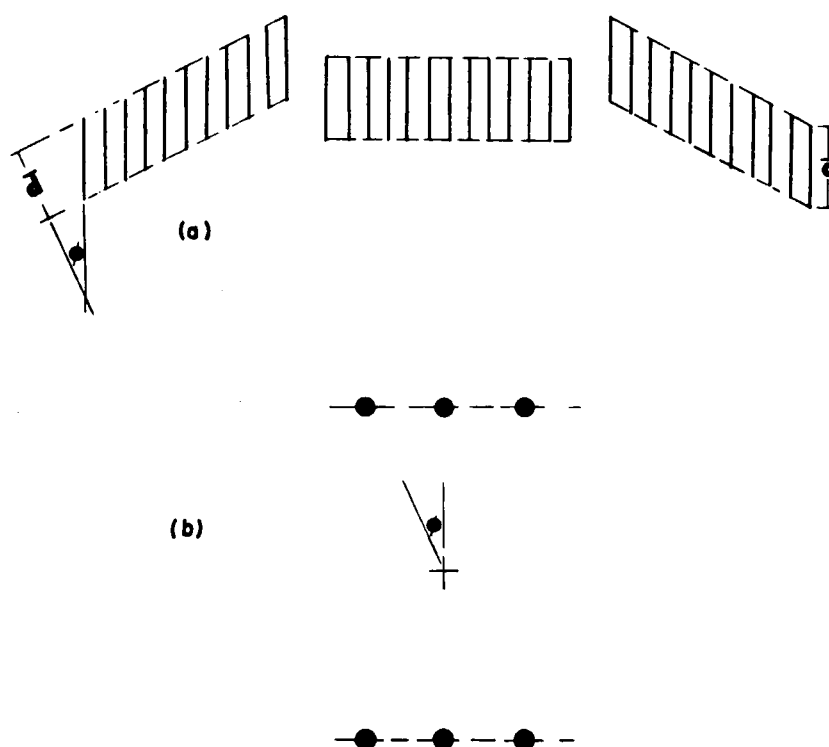


Figure 2A-5. (a) Schematic model of a lamellar structure which would produce the SAXS pattern shown in (b).

Source: J. J. Klement and P. Geil, J. Macromol. Sci. - Phys., B5, 535-558 (1971).

surface-to-surface distances d as shown in Figure 2A-5a. It can be shown that the small-angle reflection arising from the repeat distances d lies on layer lines as shown in Figure 2A-5b. The four point patterns can be interpreted as a continuous distribution of the tilted layers shown in Figure 2A-5a, with a concentration of layers tilted at the angles corresponding to the maxima in the layer lines. Rotation of the structure about a vertical axis would generate the toroidal intensity pattern discussed previously.

Fischer and Fakirov found four-point SAXS patterns for drawn and annealed PET (27). They believe the patterns are related to the macroscopic shape of the sample since four-point patterns were observed in drawn films at moderate annealing temperatures but not in fibers except at the highest annealing temperature. The responsible structure is believed to be created by "a staggering of the molecules along (100) planes." They reported that in samples with a rectangular cross section the (100) planes preferentially orient parallel to the surface while in bristles with a circular cross section a random texture is observed. Therefore no staggered conformation is developed in fibers until extremely high annealing temperatures are used.

Fakirov et al. (25) describe the microstructure present in annealed, highly oriented PET in terms of a mosaic block structure. This structure consists of a paracrystalline lattice in which the array of crystalline blocks possess both longitudinal (along the fiber axis) and lateral order. The authors believe that the lateral growth of the mosaic blocks or crystallites "is only possible by additional chain folding and staggering, since growth is hindered by chains which are already incorporated in other mosaic blocks."

B. STRUCTURE DEVELOPMENT DURING MELT PROCESSING OF PET

The cooling rate and the elongational velocity gradient are the most important factors leading to the solidification and orientation of a polymer during melt spinning (81).

Studies on the melt spinning of PET fibers have shown that the rate of crystallization depends on the winding speed (35). The density, a measure of crystallinity, was found to increase with increasing winding speed. Differential thermal analysis showed that the fibers changed from amorphous to semicrystalline over the range of winding speeds from 2000 m/min to 6000 m/min. There was a sharp increase in density from about 4500 m/min to 6500 m/min. WAXD first indicated some crystallinity in the fibers spun at 4500 m/min.

Using WAXD data from the ($\bar{1}05$) peak, the crystal orientation factor f_c was calculated. The data indicated that the molecules became increasingly aligned with the fiber axis as winding speeds increased. At 6000 m/min, f_c was 0.98, which indicated almost parallel alignment of the crystallites with the fiber axis.

SAXS measurements on samples wound at the highest speed showed no diffracted intensities. It was believed that the high rate of crystallization did not allow time for a folded-chain-type structure to form.

Amorphous orientation factors f_a were calculated using sonic moduli values, the crystal orientation factors, and the volume fraction of crystalline material (90). There was very little amorphous orientation below a winding speed of 4000 m/min. At higher winding

speeds significant orientation of the amorphous chains was achieved. At 6000 m/min, f_a was 0.69 which indicated good alignment with the fiber axis.

C. MORPHOLOGY AND MECHANICAL PROPERTIES OF DRAWN PET

Structure-Property Correlations in Drawn Fibers and Films

Studies on drawn PET fibers have shown that the modulus and tenacity improve with drawing. These changes were accompanied by increases in birefringence, the crystallite orientation function f_c , and the amorphous orientation function f_a (66). The improvement in mechanical properties was generally attributed to the increased alignment of the chains with the fiber axis.

When PET films were stretched uniaxially the tensile strength was increased substantially in the MD and only slightly in the TD. The elongation to break dropped in the MD and remained about constant in the TD. The modulus of elasticity increased in the MD and reached a minimum in the TD at a draw ratio of 4X before returning to the original value at 5X. The initial modulus, as measured by the force required to elongate the sample 5%, was seen to increase in the MD while reaching a minimum in the TD at a draw ratio of 3.5X (80).

Three structural factors are important in determining the mechanical properties of drawn film: (1) the size and orientation of crystallites, (2) the amount and direction of "trans" isomers in the amorphous region, and (3) the amount of crystallinity.

According to Heffelfinger and Schmidt (34), the following changes in morphology were believed to take place during uniaxial stretching of

unoriented PET. As the originally randomly oriented molecules were deformed, the molecular chains became partially aligned in the mill direction and some crystallization occurred. The crystallites were formed with their c-axes mostly parallel to the stretch direction. Some of the (100) planes were aligned parallel to the film surface. As the film was stretched the c-axes became more closely aligned with the MD and more of the (100) planes aligned themselves parallel to the film surface. The resulting structure had uniplanar-axial orientation as defined by Heffelfinger and Burton (32).

Warren's correction for the Scherrer line broadening equation was used to calculate average crystallite lengths (34, 44). In PET, the broadening of the ($\bar{1}05$) diffraction peak was used as a measure of the crystallite length. The crystallite length showed a steady rise from 44 Å at a draw ratio of 2X to 65 Å at 5X (see Table 2C-1). The long period, as determined by SAXS, was 107 Å at a draw ratio of 2X. At higher draw ratios, the long period remained constant at 113 Å. The long period may be thought of as the sum of the crystallite length plus the amorphous length between crystallites. In the uniaxially drawn films, the crystallite length increased from 44 Å to 65 Å over the range of draw ratios from 2X to 5X. The amorphous length decreased from 63 Å to 45 Å over the same range. Apparently the crystallites were growing at the expense of the amorphous regions during drawing. This seems reasonable since the crystallite regions can grow more easily as the alignment of the chains improves.

The amount of "trans" isomer as detected by infrared absorption techniques, is a measure of the extension of the molecules. When the

TABLE 2C-1
MORPHOLOGY OF UNIAXIALLY STRETCHED PET FILMS

Stretch Ratio	Long Period Å	Crystalline Length Å	Amorphous Length Å	Total trans %	Crystalline trans %	Amorphous trans %
As Cast	-	-	-	13	0	13
2.0	107	44	63	21	7	14
3.0	113	52	61	34	14	20
3.5	113	58	55	41	17	24
4.0	113	60	53	56	25	31
4.5	113	63	50	65	27	38
5.0	113	65	48	78	30	48

Source: Heffelfinger, C., and P. Schmidt, Journal of Applied Polymer Science, 9, 2661 (1965).

cast film is stretched the molecules become aligned and some of the individual chain segments become extended or converted from the "gauche" to "trans" form. The crystalline regions consist only of "trans" isomer.

As the chains become aligned, "trans" isomers were brought into proximity and some crystallization occurred. Beyond a stretch ratio of about 3.5X, the stress on the "trans" segments caused the phenyl rings to orient approximately parallel to the film surface. As stretching continued, the amount of "trans" segments in the amorphous regions increased more rapidly than the amount of "trans" in the crystalline regions.

The modulus and tensile strength increased dramatically in the stretch direction with stretching but changed very little in the transverse direction. The elongation to break decreased with increasing stretch ratio in the stretch direction, but remained about constant in the transverse direction (see Table 2C-2).

The amount of amorphous "trans" is a measure of the extension of the amorphous chains and, hence, can be directly related to the modulus, tenacity, and the elongation to break in the stretch direction (see Tables 2C-1 and 2C-2).

The dimensional stability and mechanical properties of the films depends on the crystallinity. Crystallization may be brought about by annealing. The effects of annealing will be discussed in a separate section.

TABLE 2C-2
MECHANICAL PROPERTIES OF UNIAXIALLY STRETCHED PET FILMS

Stretch Ratio	Modulus, psi		Tensile Strength, psi		Elongation, %	
	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.
2.0	460,000	328,000	16,900	6,470	214	497
3.0	883,000	299,000	26,000	6,540	92	490
3.5	1,018,000	265,000	31,800	7,090	68	400
4.0	1,276,000	253,000	40,800	6,520	48	474
4.5	1,546,000	303,000	47,318	7,410		
5.0	1,772,000	331,000	57,744	7,290	19	492

Source: Heffelfinger, C., and P. Schmidt, Journal of Applied Polymer Science, 9, 2661 (1965).

Effects of Annealing on the Morphology and Mechanical Properties of Oriented Samples

1. Fibers

Effect on Morphology. When oriented PET fibers or films are annealed without restraint, shrinkage occurs.

The amount of shrinkage in fibers was shown by Samuels (66) to increase with increasing annealing temperatures for a given time. The shrinkage was accompanied by a decrease in the amorphous orientation and an increase in the thickness of the crystallite.

The amount of shrinkage was proposed to be directly related to the initial structure present in the fibers after drawing. Samuels suggested that the orientation present before drawing returns along the original extension path during annealing and shrinkage, and that the shrinkage mechanism is controlled primarily by the behavior of the noncrystalline chains.

Wilson (85) investigated the relationships of shrinkage and chain folding in drawn and annealed PET fibers. Samples were annealed for one minute in oil or ten minutes in air. The shrinkage was explained in terms of rubber-like contractions.

Orientation in drawn fibers may be locked in to some extent by the crystallites, but in non-crystalline regions the orientation is frozen in at temperatures below T_g . When the fiber is heated, the non-crystalline regions unfreeze and become rubbery. The molecules become disoriented as relatively straight molecules coil up due to a tendency to assume a statistically more probable, and shorter, end-to-end distance. This effect is observed as the overall shrinkage of the sample.

The crystallinity, as measured by density, was found to be a function of the shrinkage temperature rather than the amount of shrinkage.

Wilson concludes that there is not a cause and effect relationship between chain folding and shrinkage in PET. Instead, a two-part process is involved. First there is a rapid shrinkage of the sample upon annealing, involving the relaxation of the taut amorphous regions. Then regular chain folding occurs provided temperature conditions are right and enough time is available. The folded structure could be formed by taking up slack in the disoriented amorphous regions or they may result from the perfection of paracrystalline or distorted lamellar structures.

Effect on Mechanical Properties. Mechanical properties were studied by Wilson (85) and related to annealing temperatures and amounts of shrinkage. Stress-strain curves showed a sharper yield with increasing shrinkage. However yield loads varied little with annealing temperature or amount of shrinkage. The initial modulus decreased with increasing shrinkage and increasing annealing temperature. The breaking load gradually increased with temperature up to 150°C and then dropped off sharply past 200°C.

The decrease in modulus with increasing shrinkage is consistent with the view that modulus is determined by the orientation in the amorphous regions. The fact that breaking load varied little with shrinkage at temperatures less than 200°C suggests that the structure present in the original drawn film was recovered during the tensile testing. The rapid decrease in breaking loads with annealing

temperatures above 200°C suggests that above a certain level of crystallinity the yarn is no longer redrawn during tensile testing and the orientation present in the original drawn fiber can not be recovered. The "frozen in" disorientation leads to the lower breaking loads.

Samuels (66) reported the relationship between the annealing temperature and the tenacity of PET fibers. A maximum in the tenacity was observed at approximately 100°C. The maximum was explained by the morphology of the sample. As the samples were heated, free shrinkage occurred as a result of the relaxation of the strained, oriented, noncrystalline chains. At higher annealing temperatures more shrinkage was possible. Since the tenacity is dependent on the amorphous orientation, lower tenacities would be expected from samples relaxed to lower orientation states.

2. Films

Mechanical Properties. Fibers or films can be annealed in either of two ways: "free annealed" (no restraint) or under tension. Heffelfinger and Schmidt (34) chose to heat set their drawn films under tension. Samples shrank varying amounts depending upon the tension. Mechanical properties were then reported as a function of shrinkage due to annealing.

The stress required to elongate the film 5% after annealing decreased from about 32,500 psi at 0% shrinkage to about 18,000 psi at 16% shrinkage for films initially drawn by 4.5X. This compares to a value of 33,350 psi for the films before annealing.

The elongation to break increased from about 25% for films that were not allowed to shrink any, to about 45% for films which shrank 15%.

The change in mechanical properties with the degree of shrinkage is explained as being due to a decrease in molecular orientation, as is the case for fibers. Heffelfinger suggests that "the orientation stresses are so great that they can not be completely restrained by tension on the film during crystallization so that stress decay, localized melting, and recrystallization occur." This "structural relaxation" as he calls it, is reflected in several ways. As the amorphous chain segments coil and fold into a more compact structure the amorphous length is decreased (as evidenced by a decrease in the long period), the density increases, and the elongation to break decreases.

Morphology. Heffelfinger and Lippert (33) have studied oriented PET films deformed by two paths. The first path involves spherulitic crystallization caused by heating before stretching. The second path involves stretching the amorphous film followed by heating under tension at 140 - 150°C. Orientation by Path I involves spherulitic deformation and the fragmentation of the folded chain lamellae that occur in the spherulite. Path II is the rearrangement of the molecules from the liquid-like, glassy state.

SAXS and WAXD offer evidence for the existence of three types of structured domains. The smallest involves crystallite unit cell planes and axes (5 - 15 Å). Next are domains having a periodicity of 100 - 150 Å. The morphology of these is uncertain. The largest are proposed

to be platelets or sheet structures. These domains are on the order of 290 Å to 3800 Å thick and 2000 to more than 10,000 Å long. Similar structures are obtained for both paths. This indicates that the molecules aggregate in a preferential manner under stress so that the final structure is independent of the deformation and crystallization path used.

The effect of annealing is to reduce the size of the intermediate sized structure while increasing the crystallinity. Free shrinkage for samples drawn 25% is about 40% when annealed at 200°C for five minutes.

D. ROLLING OF AMORPHOUS POLYMERS

Since little is known about the effects of rolling PET we shall see how rolling affects the properties and structure of other polymers. Both amorphous and crystalline polymers were studied since PET can occur in either form. In this section the previous research on amorphous or "essentially" amorphous polymers is summarized.

Effect on Mechanical and Physical Properties

Gruenwald (31), Broutman and Patil (12), Broutman and Kalpakjian (10), Litt and Koch (47), Bahadur and Henkin (3) and Gezovich and Geil (29) have studied the effects of rolling on the mechanical properties of various amorphous and semi-crystalline polymers such as polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), Polyvinyl chloride (PVC), polysulfone (PSF), polyphenylene oxide (PPO), and amorphous poly(ethylene terephthalate) (PET).

All the above polymers showed a general increase in the tensile

strength and modulus of elasticity in the RD with increased levels of roll reduction. All samples showed the typical cold drawing phenomenon in the unrolled case. With increased roll reductions, the yield strength generally increased while the yield point became less conspicuous in the RD. At high roll reductions a yield point was no longer observed.

In PC, PPO, and PET, the elongation to break generally decreased with increased rolling to a value less than half that of the unrolled sample. In polysulfone, a small reduction caused the ductility to increase drastically. Upon further rolling the elongation to break gradually decreased. The elongation to break in PVC was observed to increase with rolling up to a maximum and then fall off. Unlike the other polymers, ABS showed a general increase in ductility with increased roll reductions. Broutman and Patil (12) believe this behavior may have been due to surface flaws in the specimens which caused a premature break. They also reported no stress whitening in ABS during tensile testing beyond about 40% cold work.

For ABS, PC, and PVC there was a gradual decrease in the yield strength in the TD and a less pronounced yield point with increased rolling. No appreciable change in the tensile strength as a result of rolling occurred in the transverse direction for these polymers. The drawing stress was reduced in the TD while the elongation to break increased as the roll reduction increased (10, 12).

In PET the modulus, yield strength, tensile strength, and the elongation to break were all higher in the TD at a roll reduction of $t/t_0 = 0.3$, than at $t/t_0 = 0.44$.

Rockwell hardness tests were performed on amorphous polymers by

Broutman and Patil (12). Results were plotted as a function of the percent reduction in thickness. PC, PPO, and Noryl (modified PPO) had similar values and were plotted as one curve. For relatively softer plastics such as ABS and high impact PVC, the depth of penetration was plotted instead of hardness.

All polymers showed a minimum hardness at about a 20% reduction in thickness. Beyond 20%, the hardness approached the original value. Hence, these curves pointed out the peculiarity that these polymers initially soften upon rolling.

The toughness of PC samples was measured by performing Izod impact tests. "Impact strength" was plotted as a function of roll reduction. There was a sharp increase after a 5% reduction in thickness. With more rolling, the "impact strength" dropped slowly. At a 50% reduction, the "toughness" had decreased back to its original value. It was shown that samples cut at 45° and 90° to RD had a greater "impact strength" than samples cut in the RD, provided the roll reduction exceeded 30%.

For unrolled polycarbonate there was a "thickness transition effect" at about 0.180 inches. Below 0.180" the "impact strength" was approximately 18 ft·lb/in, but above 0.180" the value dropped to 3 ft·lb/in. Rolling, however, allowed high "impact strengths" to be maintained regardless of the thickness (12).

An increase in density with rolling has been noted for some amorphous polymers: PC, ABS, polysulfone, PPO, and Noryl. No results were given for PET. The increase is believed to be caused by a decrease in the free volume. However, care must be exercised in this

interpretation since some of these polymers such as polycarbonate have the potential for slight crystallization.

Bahadur and Henkin (3) noted a small decrease in the density of PVC upon rolling. Since x-ray measurements did not show any crystallinity, the decrease was attributed to "the rearrangement of the molecules arising from deformation if the rolling operation."

Effect on Orientation and Morphology

There is very little data in the literature on the effects of rolling on the chain orientation of amorphous polymers.

The paper by Broutman and Patil (12), however, showed photoelastic fringe patterns (which are related to birefringence) in uniaxially rolled amorphous polycarbonate sheets at different degrees of rolling. At low deformations (<20% reduction), the fringe patterns indicated no significant orientation of the chains. At higher reductions the chains began to orient in the roll direction with orientation increasing with greater roll reductions.

Based on work done by Samuels (65) on fibers, Broutman and Patil believe that up to a 20% roll reduction, transverse "macrocracks" are formed. Beyond about 20%, the large macrocracks yield and produce many smaller voids elongated in the roll direction. The formation of the microvoids is linked by birefringence to the beginning of chain orientation.

The orientation of the chains was associated with a decrease in cold drawability and elongation to break. The increase in tensile strength was also explained in terms of chain orientation.

The morphology of rolled amorphous PET was investigated by Gezovich and Geil (29) using WAXD techniques. Two strong but diffuse reflections were observed on the equator, while two weak but relatively sharp meridional reflections, believed to be the (001) and (003) reflections, were observed. The authors believed the WAXD patterns indicated a preferential alignment of the chains with the roll direction, but with the benzene rings "not in register." The benzene rings in adjacent chains, apparently, did not show any particular periodicity along the roll direction. The alignment was not perfect and was said to resemble a "liquid crystal" type of structure.

When the samples were annealed at 180°C , they gave sharp WAXD patterns. The authors found these patterns to be similar to those of drawn and annealed PET, indicating a strong alignment of the chains with the roll direction.

SAXS patterns could not be obtained for rolled PET before annealing. After annealing highly rolled PET ($t/t_0 = 0.3$), a four point pattern was observed. This pattern was attributed to crystal lamellae arranged in two specific orientations.

Effects of Annealing

1. Effects on Ductility

Bahadur and Henkin (3) annealed rolled PVC and PC and other polymers at a temperature just below their melting point. They found that such annealing treatments invariably decreased the ductility of the rolled material. No data was given for other mechanical properties. The decrease in ductility was attributed to the formation and/or increase in crystallinity.

2. Effect on Thermal Stability

Cold rolled polycarbonate, polysulfone, and other amorphous polymers will shrink toward their original dimensions if they are heated to their glass transition temperature (T_g) or above. In polysulfone, the percent recovery increases gradually with temperature for temperatures more than 35°F below T_g . As temperatures approach T_g , the percent recovery increases sharply with increasing temperature. Near T_g , the thermal agitation is great enough to overcome the van der Waals forces which freeze in the chain orientations and the molecules are able to slip back toward their original conformations (11).

E. ROLLING OF CRYSTALLINE POLYMERS

Effect on Mechanical and Physical Properties

1. Polyoxymethylene

Mechanical testing was performed on uniaxially rolled POM by Gezovich and Geil (29). An increase in tensile strength and yield strength with rolling was observed in the RD, but was accompanied by decreases in the TD.

For samples rolled to a t/t_0 (thickness after rolling / original thickness) of 0.4, both the stress at break and the strain to break were greater in the RD than in the TD. The RD samples yielded, necked until fully drawn, and then broke, while TD samples tended to break shortly after yielding. This is in contrast to most polymers.

2. Polyethylene

Meinel and Peterlin (53) have studied the effects of rolling on polyethylene. The mechanical properties were measured at -196°C . The elastic modulus increased with rolling to a value over twice that of the unrolled specimen. The tensile strength increased by a factor of three when samples were highly rolled.

Both the density and heat of fusion were found to decrease with rolling for samples which were quenched from the melt or annealed prior to rolling.

The decrease in density and heat of fusion was explained as being caused by the formation of microfibrils having a lower density because of the higher paracrystalline disorder of the fiber structure. A small amount of the change was attributed to the appearance of a monoclinic phase.

3. Polypropylene

Cold rolled polypropylene has been studied extensively by Wilchinsky (83, 84) and by Vijay Dhingra at the University of Tennessee at Knoxville (16). Uniaxial rolling at room temperature increased the yield strength in the RD but caused a decrease in these properties in the TD. The modulus of elasticity was increased in the RD, TD, and at 45° to the RD, but the largest improvement was noted in the RD. Dhingra found that small roll reductions greatly increased the elongation to break in all directions tested. At higher reductions the elongation to break decreased, falling off most rapidly in the RD.

Wilchinsky found that, in general, polypropylenes with lower

density and lower melt indices were less brittle. The effect of cold rolling was to reduce the brittleness of samples cut with their major axis along the roll direction. The brittleness of samples cut parallel to the TD seemed to be independent of the degree of rolling.

Dhingra found the density to decrease upon rolling. This was thought to be caused by the destruction of crystal structure.

4. Crystalline Polycarbonate

Kabayashi and Broutman (45) crystallized polycarbonate sheets by both thermal and vapor sorption techniques.

The unrolled, thermally crystallized samples showed a slight increase in modulus over the unrolled amorphous sample, but the elongation to break was reduced from 109% to only about 2% and the tensile strength was reduced somewhat. Since thermal crystallization caused the samples to be brittle and relatively weak, further investigations were focused on the samples crystallized by the acetone vapor sorption method.

The modulus of elasticity increased slightly in the RD with rolling. The tensile strength increased from about 10,400 psi at 25% reduction in thickness to about 24,000 psi at a 69% reduction. The elongation to break in the RD was greatest at a 50% roll reduction.

The modulus of elasticity and the tensile strength were less in the TD than in the RD but the elongation to break was much greater in the TD.

The tensile strengths both in the RD and TD for the rolled crystallized samples do not appear to be much different than the values reported in an earlier paper (11) for rolled amorphous samples.

The results, however, are confused by the effect of residual acetone. After rolling, the acetone content can be reduced by heating, but ductility is lost and the polymer becomes more brittle.

5. Poly(ethylene terephthalate)

A patent issued by the DuPont company in 1959 (48) discussed the invention of a process to orient crystalline PET film by rolling. The process involved rolling unoriented crystalline PET having a density of at least 1.36 gm/cm^3 with heated rolls having a temperature between $150 - 190^\circ\text{C}$. The process not only oriented the film but also gave it thermal stability.

Films having a density of 1.36 could not be rolled below 100°C without shattering due to their brittleness. Rolling above 190°C caused the film to stick to the rolls. Rolling below 150°C gave the films a relatively low thermal stability, so the preferred temperature range for rolling the unoriented crystalline PET was in the range of $150 - 190^\circ\text{C}$.

The films were rolled in two directions since a film was desired having equal mechanical properties in both directions of rolling. The high temperatures of rolling were desirable since crystallization helped "lock in" the orientation imparted to the film in the first rolling direction so that it would not be lost upon rolling in the second direction.

The actual temperature of the film in the nip of the rolls was probably higher than the surface temperature of the rolls because of the mechanical energy transferred to the film during rolling. All the films were at room temperature prior to rolling.

Mechanical testing was performed on the samples after cross rolling. The tensile strength was based on the initial cross-sectional area. The mechanical properties were determined at an elongation rate of 100% per minute. The modulus was determined at 1% elongation. Thermal shrinkage was measured after free annealing for one half hour at 150°C.

In Table 2E-1 the mechanical properties of various rolled PET films are shown. Control A is unrolled, amorphous film. The other samples were crystallized at 130°C for 5 minutes producing a density of 1.36 gm/cm³. Control B was rolled at 115°C - below the critical range of 150 - 190°C. These films were passed between rolls 4.625" in diameter rotating at about 2 RPM. The thickness reduction ratio was around 0.6 for each rolling direction. Tenacity was more than doubled in each direction. Modulus increased from 300,000 psi for the amorphous sample to between 400,000 to 550,000 psi for the cross rolled samples. Elongation to break dropped from 450% for Control A to around 100% in both directions for the other samples. Thermal shrinkage was greater than 5% for Control B, but dropped to less than 3% for samples rolled at 150°C and to around 1.5% for 190°C.

Some samples were crystallized under a pressure of about 1200 psi to a density of 1.3705 gm/cm³ and then rolled in one direction only. The density increased to 1.3787 upon rolling. This was probably due to crystallization since the rolls were heated to 160°C. At a thickness reduction ratio of 0.60 the following mechanical properties were reported. The tensile strength had increased to 25,600 psi in the RD

TABLE 2E-1
MECHANICAL PROPERTIES OF VARIOUS PET FILMS

Example	Original Thickness (mils)	Final Thickness (mils)	Roll Temperature °C	Thickness Reduction Ratio	Tenacity psi		Elongation Percent		Modulus psi		Thermal Shrinkage Percent
					MD	TD	MD	TD	MD	TD	
				First Dir. Rolling							
Control A	50.0				8,000	8,000	450	450	300,000	300,000	Became embrittled during test
Control B	18.6	2.6	115	0.650	22,900	16,600	118	92	494,000	420,000	>5
1	45.0	5.7	150	0.633	22,100	23,400	141	101	443,000	527,000	2.8
2	66.0	8.4	150	0.666	18,200	17,900	104	91	476,000	439,000	2.9
3	45.0	6.2	190	0.666	23,100	17,200	99	64	520,000	426,000	1.5
											1.2

Source: Christian Bent Lundsager, U.S. Patent 2,899,713 (1958).

and decreased slightly to 7,200 psi in the TD. The elongation was 68% in the RD and 32% in the TD. The modulus increased to 820,000 psi in the RD and 340,000 psi in the TD. The shrinkage was 0.6% in the RD and 0% in the TD.

The films were slightly hazy to opaque, depending on the degree of crystallinity, before rolling. The patent claimed the rolling process produced oriented films which were highly crystalline yet highly transparent.

An advantage of the process, the patent claimed, was its "orientation efficiency." They explained that to obtain equivalent mechanical properties by conventional two-way stretching processes, the film thickness must be reduced, and the length and width increased, to a greater degree than when orientation is obtained by rolling in two directions. Hence, it was easier to orient thick films by rolling. Desired properties were reached at a lower degree of thickness reduction by rolling than with stretching.

Another patent (23) reported the mechanical properties for PET strapping made by a rolling process. One strap was rolled at 150°C to 3.57 times its original length. The width decreased during rolling to 0.88 times the original dimension. A tensile strength of 37,900 psi was obtained in the RD and 7,880 psi in the TD. An elongation of 4.65% was obtained when the sample was subjected to a stress of 35,000 psi. After the stress was reduced to 17,500 psi, the elongation remained at 1.2%. It was preferred that the strapping return to within 2% of its original dimension after being stretched so that it would remain tight about whatever container it was used to bind.

A tensile strength of at least 40,000 psi was desired in addition to the "tightness" requirement in order for the PET strapping to compete with steel. These conditions could only be met at higher roll reductions.

Effect on Orientation and Morphology

1. Polyoxymethylene

The orientation and morphology of POM was investigated by Gezovich and Geil (28) using wide angle and small angle x-ray techniques and electron microscopy.

The polymer consisted initially of spherulites with an overall random distribution of lamellae. Wide angle x-ray diffraction (WAXD) pole figures of uniaxially rolled samples showed that the molecular chains preferentially tilted at about 30° to the RD at moderate roll reductions, and aligned in the RD at higher roll reductions.

The predominant feature of the SAXS patterns was a well defined four-point pattern when the beam was parallel to TD. This indicated the lamellae had oriented themselves in two directions symmetrically about the RD.

Gezovich and Geil believe the lamellar tilt was caused by tensile and shear forces exerted by the rolls. The shear force was distributed through the sample such that maximum stress was exerted at the surface and maximum velocity occurred at the center. This, they say, explains the characteristic V-shape between the lamellae.

The SAXS patterns showed a continuous decrease in lamellae tilt (the angle between the lamellar faces and the RD) from 40° at $t/t_0 = 0.8$ to less than 25° at $t/t_0 = 0.3$. The long period decreased slightly

down to a thickness reduction of 0.5. Between 0.5 and 0.4, a sharp decrease was observed. Beyond 0.4, the long period remained at about $140 \text{ \AA}$. Combined with the results from WAXD, these results indicated that the chains must tilt within lamellae. At very high roll reductions, SAXS patterns indicated a partial breakup of the lamellae. A schematic model was presented to show the presumed effects on lamellar and chain tilt (see Figure 2E-1).

Electron microscopy showed a "zig-zag" pattern of striations on the surface of a fracture lying in the plane of the film rolled to $t/t_0 = 0.8$. The width of the striations was about $400 \text{ \AA}$, while small angle spacing indicated a periodicity of about $190 \text{ \AA}$. The authors suggested that the striations were probably stacks of lamellae rather than individual lamellae. The lamellar tilt, as measured from the micrographs ranged from 45° to 55° , while SAXS indicated a tilt of about 43° .

Starkweather, Wilson, and Clark (72) studied the orientation of rolled POM at very low deformations (extended in length by 1.2X). They found that the first preference for orientation of the crystals is one with the chains oriented perpendicular to the roll direction, not parallel. Since some portions of the spherulites had their lamellar crystallites parallel to the roll direction and since the c-axes were perpendicular to the lamellae, these chains would be oriented in or close to the transverse direction. Thus, the authors proposed that rolling causes the crystallites to rotate so that the c-axes align into a more uniform transverse orientation.

It is of interest to note that up to a 40% increase in width can

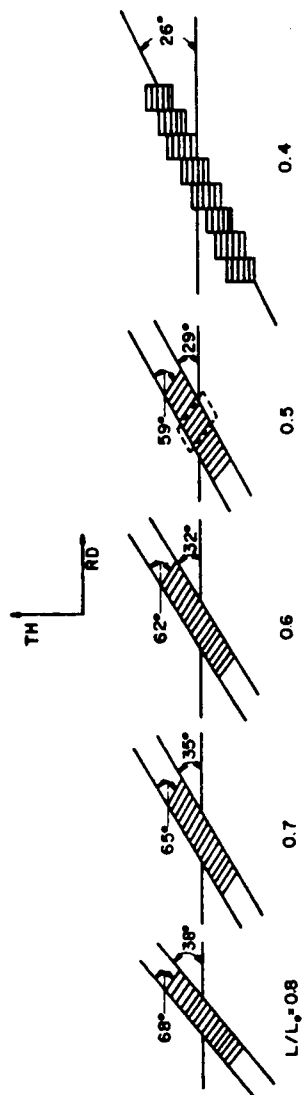


Figure 2E-1. Schematic model depicting the effects of rolling on the lamellar and chain tilt in POM. TH is the normal direction, RD is the roll direction, and L/L_0 is the thickness direction.

Source: D. Gezovich and P. Geil, *J. Materials Sci.*, **6**, 509-530 (1971).

occur in uniaxially, highly rolled POM. An increase in width has been noted for other polymers, but this is not a general phenomenon in rolled polymers. Instead, it depends on the polymer (28, 29).

2. Polypropylene

Dhingra (16) has studied the effects of cold rolling on the chain orientation and morphology of PP using WAXD pole figures, SAXS patterns, and electron microscopy. At low deformations (<50% thickness reduction) the small angle "long period" decreased steadily with rolling, while WAXD pole figures showed that the molecular chains became oriented at approximately 30° to the RD. At higher roll reductions the long period decreased rapidly and the chains preferentially oriented in the RD. The lamellar tilt, as measured from SAXD patterns, remained constant up to about a 60% thickness reduction, and then increased with additional rolling. The increase in lamellar tilt plus the sharp decrease in long period indicated that some type of lamellar breakup was occurring. Dhingra proposed that the following structural changes occurred. At low deformations the chains tilted and slip occurred within the lamellae. At high roll reductions, the lamellae broke up and the chains were drawn out parallel to the RD. Figure 2E-2 is a schematic model showing these changes. This model is similar to that proposed by Gezovich and Geil (29) for polyoxymethylene.

The tensile properties were shown to be consistent with the structural changes. The tensile strength, yield strength, and modulus will be higher along the chain axis than perpendicular to it. Thus, the increased alignment of the chains with the RD explained the increase in

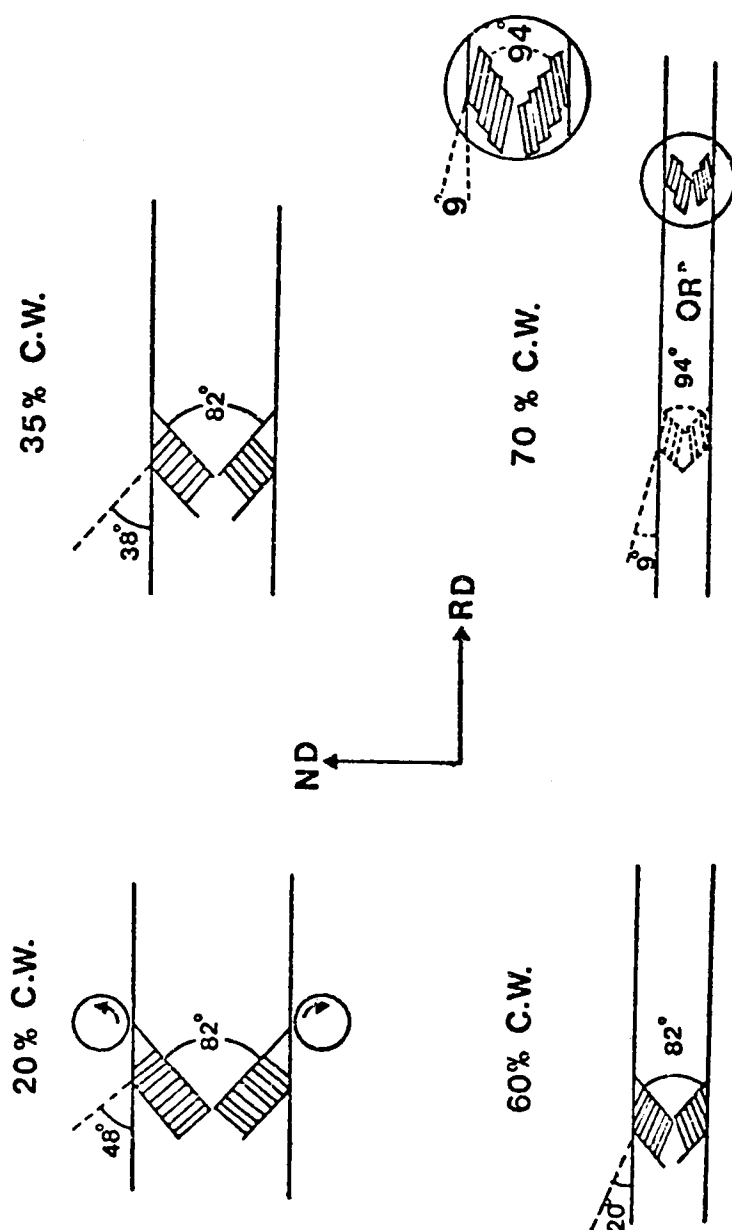


Figure 2E-2. Schematic model showing the effects of uniaxial rolling on the lamellar and chain tilt in polypropylene.

Source: V. J. Dhirgra, J. E. Spruiell, and E. S. Clark, Poly. Engr. Sci., 21, 1063-1071 (1981).

mechanical properties in the RD and their decrease in the TD. The increase in elongation to break at low deformations was not entirely understood. Dhingra speculated that the lamellae perpendicular to the RD tilted toward the RD with rolling, thereby facilitating lamellar break-up during the extension of the tensile test and increasing elongation to break. The elongation to break decreased at higher reductions and was smaller in the RD because of the previous extension by rolling.

3. Polyethylene

Cold Rolling. The morphological changes that occurred in low molecular weight PE upon rolling, as observed by SAXS, were reported by Meinel and Peterlin (53) as follows. The disappearance of meridional scattering in patterns taken with the x-ray beam perpendicular to RD, indicated the lamellae perpendicular to the RD were either being destroyed during rolling, or more probably, the lamellae were being rotated toward the RD. In the same patterns, the equatorial scattering disappeared at a low roll ratio with the x-ray beam parallel to the TD, and at a much higher roll ratio with the beam perpendicular to the plane of the film. According to Meinel and Peterlin, this indicated that platelets parallel to the rolled surface were destroyed before those perpendicular to the surface.

At low deformations, the chains must have tilted within the lamellae since the long period calculated from the equatorial scattering showed a decrease in thickness. At slightly higher reductions, a new two-point pattern was observed along the meridian which corresponded to the appearance of microfibrils.

At low roll reductions, thermograms indicated that the crystal size distribution had changed very little. This corresponded with SAXS patterns which showed little destruction of the original spherulites. At high reductions, however, destruction had become very evident. The thermograms indicated the formation of new crystallites with a thickness of about $100 \text{ \AA}$. They also indicated the formation of new tie molecules in the quenched samples. The dependence of the thermograms on the thermal history of the sample at low deformations indicated the incomplete transformation of the original material into the final fiber structure. With high molecular weight PE ($M_n \approx 1.4 \times 10^6$), the tilt angle of the lamellae increased with increased rolling. There was an orthorhombic symmetry in the rolled samples with the lamellae parallel to the TD. This agreed well with the reduction of thickness with little change in the width (<2%). Deformation must have occurred primarily in a plane perpendicular to the film surface and parallel to the RD. The lamellae were stacked in the RD as indicated by SAXD. A thickness of $150 \text{ \AA}$ was reported.

The new lamellae formed by rolling were independent of the thermal history of the film, unlike the low molecular weight PE. There was some indication in the thermograms of a new crystalline size. The orientation of the crystallites for the highly rolled high molecular weight PE was similar to that of the low molecular weight PE at lower reductions. In both materials, the c-axis was oriented in the roll direction and the a-axis was oriented in two directions: one normal to the rolled surface and the second at about 60° to the normal.

Hot Rolling. Yoda and Kuriyama (92) reported the following results for hot-rolled PE. The c-axis tended to align itself at 24° to the RD at low reductions and at 13° for somewhat higher reductions. Further rolling reduced the angle to 0° . They postulated that a shear deformation was occurring through a slip mechanism with the slip being (100) [001]. This was evidenced by crystallite orientation being accompanied by a decrease in the size of the crystallites. At low roll ratios the slip occurred within the crystallites (intracrystalline slip). At high roll ratios, no further degradation of crystallites was observed, so the slip mechanism here must be largely between the crystallites (intercrystalline slip).

4. Poly(ethylene terephthalate)

Very little information could be found on the morphology of rolled crystalline PET. One patent did, however, mention a rolling process to produce a uniplanar, axial oriented crystalline PET product suitable for use as strapping (23). It was desired to orient the crystals so that the 001 direction lay within a narrow angle from the RD in order to obtain the properties most useful for strapping. Maximum deformation was not necessarily the best, since this resulted in undesirable properties such a tendency to split, fibrillate, or form a "hairy" surface.

PET was one of several polymers studied for this process. The author reports that, in general in the rolled polymers, the chain axis was oriented parallel to the RD and some crystal plane had oriented so that it lay parallel to the rolled surface.

Effect of Annealing

1. Polypropylene

Cold Rolling. According to Dhingra (16), annealing caused little change in the unit cell orientation, but the lamellae reoriented significantly. Before annealing, lamellae were tilted at about 47° to the RD. During annealing, the lamellae became well aligned with the RD. Increasing the annealing temperature sharpened the texture of the samples and the long period increased.

Free annealing (without restraint) resulted in large decreases in the ductility, yield strength, tensile strength, and modulus, while fixed annealing increased the tensile strength, yield strength, and modulus, but decreased the ductility (brittle fracture was observed in the TD).

The differences were explained by Dhingra as follows. During free annealing the crystalline orientation does not change much but the macroscopic length of the sample is reduced considerably as a result of the recoil of the molecular chains in the amorphous regions. During subsequent mechanical testing, the chains in the amorphous regions elongated at low stress and reduced the strength properties. Since amorphous chains could not recoil during fixed annealing, the mechanical properties reflected their taut state.

Hot Rolling. Hot rolling produced results which were similar to a combination of cold rolling and annealing at high roll reductions. The morphology was essentially the same for both methods. The

mechanical properties for hot rolled samples were comparable with those of the cold rolled samples with subsequent fixed annealing treatments (16).

2. Polyoxymethylene

Gezovich and Geil (28) found annealing caused some dimensional recovery to occur in all samples, with higher temperatures resulting in greater thickness recovery. SAXS patterns indicated that samples annealed at different temperatures differed in their long period but not in lamellar orientation. Annealing did not remove the surface irregularities observed in the electron micrographs.

SAXS showed that lamellar orientation changed significantly upon annealing (although the orientation seemed to be independent of annealing temperature), while WAXD patterns indicated little change in the molecular orientation. For example, for a sample rolled to $t/t_0 = 0.55$ the lamellar tilt was 30° for the unannealed samples, while the sample annealed at 155°C showed a tilt of 40° . Molecular tilt remained at 30° to the RD upon annealing. This suggested the effect of annealing was to rotate the lamellae by increasing the angle between the surface of the lamellae and the chain axes (see Figure 2E-1, page). Thus the angle between the chains and the lamellar surface approached a more natural value of 90° . In this case the angle went from 60° to 70° upon annealing.

SAXS patterns of annealed samples showed that the lamellar breakup, which leads to a fibrillar morphology (seen as the meridional reflection in the observed six-point SAXS pattern), probably occurred to a small extent even at low deformations.

This literature survey has been an attempt to summarize pertinent information on drawing of PET and rolling of both amorphous and crystalline polymers. This existing knowledge should provide a basis for understanding the morphological and mechanical changes which occur in PET during rolling.

The next section explains the different methods by which PET was rolled and processed for this research and details the various techniques used to investigate the changes which occur during rolling.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. SAMPLE PREPARATION

Material

Poly(ethylene terephthalate) sheets containing approximately 0.5 wt. % TiO_2 were kindly supplied by C. J. Heffelfinger of E. I. du Pont de Nemours and Company. The sheets were approximately 2.5 mm thick and 28 cm long by 22 cm in width. Density and WAXD patterns showed that the sheets were essentially amorphous and unoriented. The number average molecular weight $\bar{M}_n$ was reported by Heffelfinger to be approximately 15,000 gm/mol.

Rolling Procedures

Rectangular pieces of film about 11 cm x 9 cm x 2.5 mm were rolled to various thicknesses. The films were passed between rolls 10.3 cm in diameter rotating at about 37 RPM. As described in the next section, rolling was carried out in most cases with the samples and rolls initially at room temperature. The samples were reduced in thickness gradually in a number of passes, with the rolls being brought together approximately 0.005" per pass. The samples were flipped over and reversed end-for-end between passes to insure a more uniform deformation. The samples were allowed to cool between passes to eliminate heat build-up and possible annealing effects.

The roll reduction was defined initially as the final thickness divided by the original thickness (t/t_0). But then it was discovered

that the width sometimes decreased with no significant change in thickness, so the roll reduction was redefined as the final cross sectional area divided by the original cross sectional area (A/A_0).

Some samples were "hot rolled." In these instances the samples were heated to a preset temperature in an oven before passing through the rolling mill. The details of this procedure are described in the next section with the description of Path IV processing.

Processing Paths

PET was chosen for this project because of its unique characteristics. It could be easily obtained in either amorphous or crystalline forms prior to rolling. This made it possible to study and compare the effects of rolling on both a crystalline polymer and an amorphous polymer without having to consider different polymers. Also, its chemical structure and low molecular weight made it substantially different from aliphatic addition polymers such as polyethylene and polypropylene.

Four processing paths were investigated. These are illustrated in Figure 3A-1 and discussed in the following sections.

1. Path I: Rolling Amorphous Film

Amorphous films were rolled as received at 25°C (room temperature).

2. Path II: Crystallization at 150°C, Followed by Rolling

PET films were sandwiched between 1/8" thick aluminum sheets and placed in an air oven. The oven had been held at 150°C overnight to ensure that thermal equilibrium had been reached. Two one-kilogram

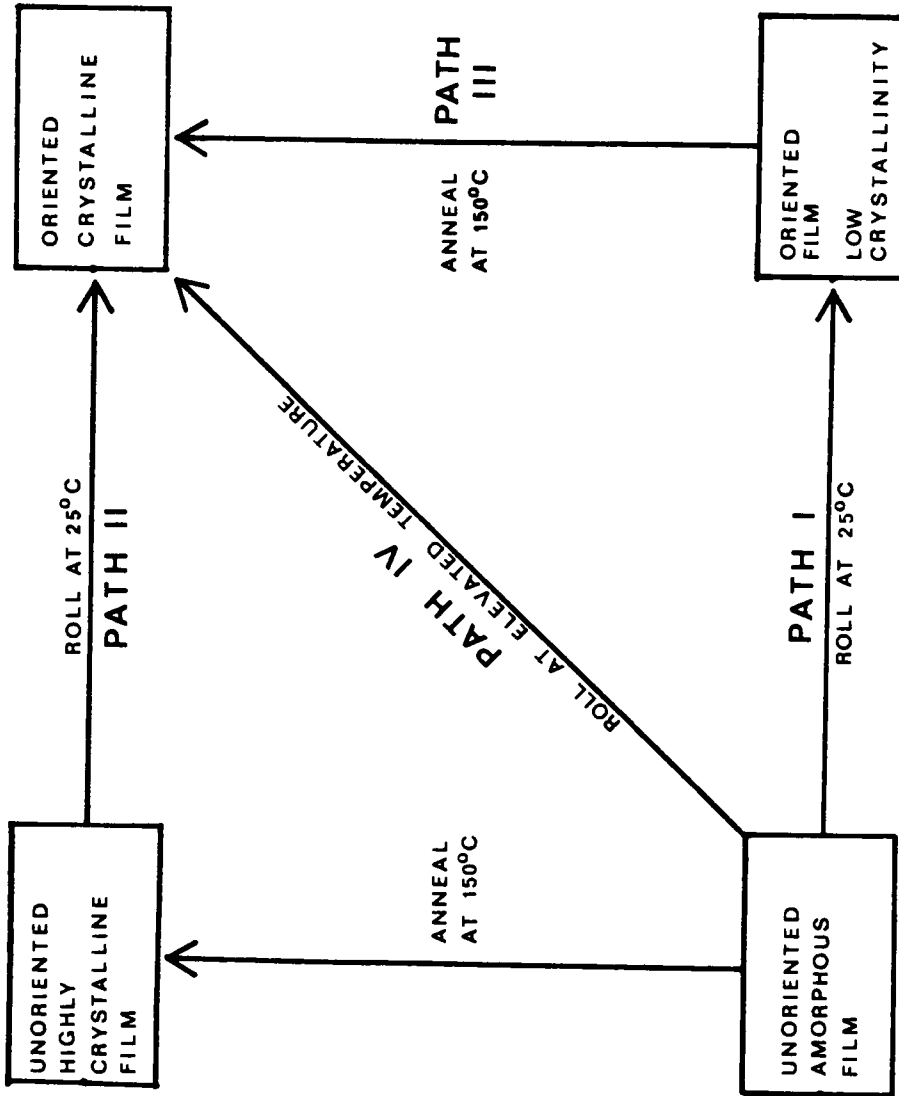


Figure 3A-1. Schematic diagram of the four different processing paths.

weights were then placed on top of the samples to prevent any distortion in the plane of the film as they passed through the rubbery state during annealing. Any curvature in the crystalline samples caused them to shatter upon rolling. The films were then annealed at $150^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 12-15 hours. This temperature was high enough to insure a high level of crystallinity without causing appreciable degradation (33, 71). The length of time was many times the half-time of crystallization so that a relatively constant level of crystallinity was reached. Tests performed at 120°C showed that almost all crystallization occurred during the first half hour (see Figure 3A-2). These highly crystalline PET samples were then rolled at 25°C .

3. Path III: Rolling Amorphous Film, Followed by Annealing at 150°C

Amorphous samples were rolled as in Path I. The resulting films were cut into strips of a suitable size for tensile testing, and annealed for two hours under pressure in a hot press at $150^{\circ}\text{C} \pm 3^{\circ}\text{C}$. Enough pressure was applied to prevent appreciable shrinkage and wrinkling from occurring. This procedure was adopted because an annealing frame which grips the sample at its edges proved to be inadequate for these polyester samples. As the samples passed through the rubbery state, the frame lost its grip and the film pulled out of the frame as it shrank. Also, flat samples were essential for subsequent tensile testing.

Some films were annealed without restraint. Density measurements and x-ray patterns were made with these samples, but tensile testing was impossible.

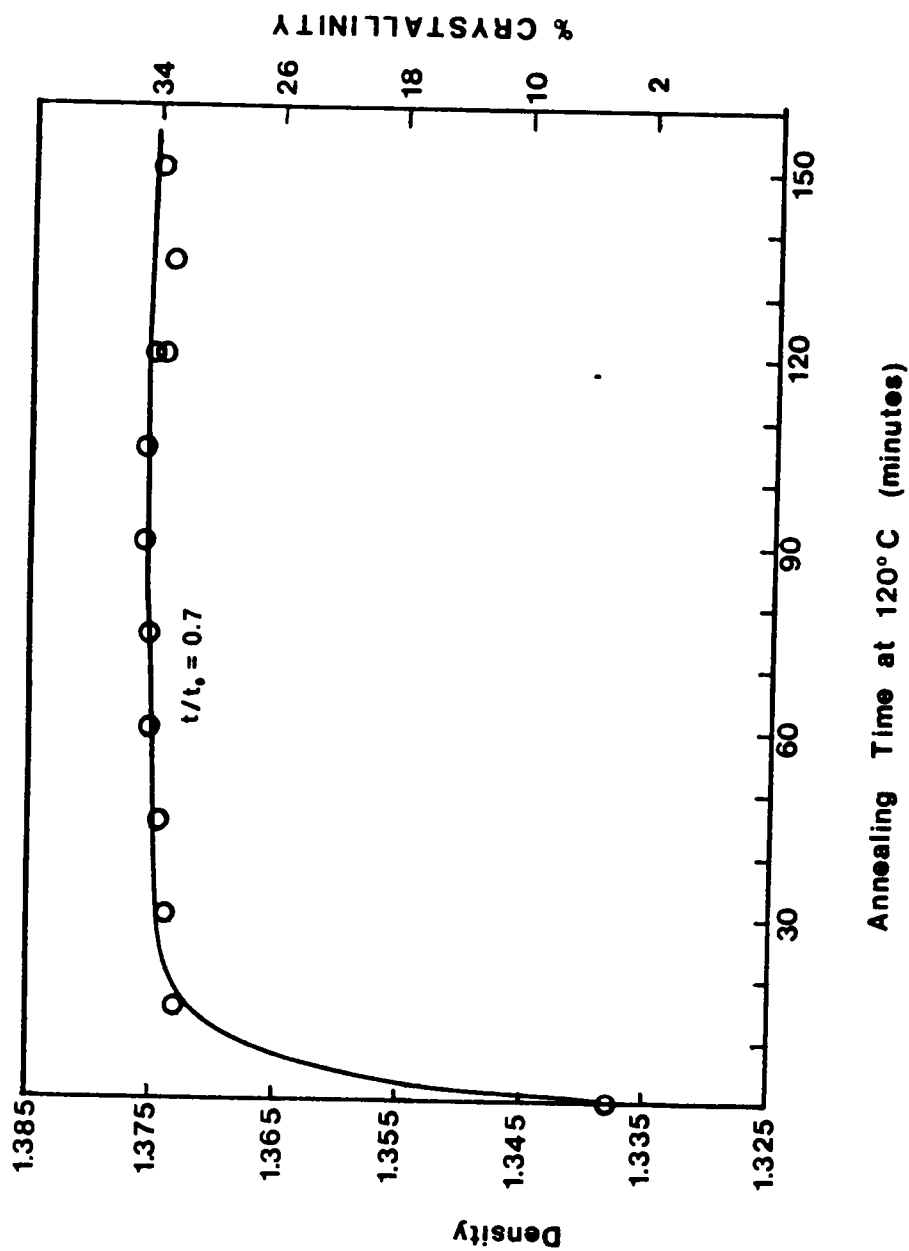


Figure 3A-2. Degree of crystallinity as a function of annealing time.

Path IV: Hot Rolling

An attempt was made to simultaneously roll and crystallize the films. The rolls were heated to about 40°C with a hot air gun. Samples were heated in an air oven at certain temperatures for five minutes, passed through the rolls several times, and returned to the oven. The samples were allowed to reheat for approximately one minute before making another pass. The total time, starting when the sample was placed in the oven, was not allowed to exceed ten minutes.

In an effort to speed up the rolling process, to reduce cooling effects and offset dimensional recovery of the samples, larger thickness reductions per pass were made for this path than for the other paths.

In order to determine the best temperature at which simultaneous rolling and crystallization could be achieved, different sets of samples were rolled at four different temperatures. Samples were not rolled below T_g since very little crystallization would occur. Above about 140°C, the half-time of crystallization was so short, the samples would crystallize before rolling. So, the temperatures of 80°C, 100°C, 120°C, and 130°C were chosen. The actual oven temperatures were slightly different since it was difficult to set an exact preselected temperature.

The actual sample temperatures were affected by several factors. The loss of heat from the oven upon opening the door caused temperatures to vary between samples within a given set. This effect was minimized by placing the samples on a thick (3/8") slab of aluminum and covering with a 1/8" thick sheet of aluminum. The temperature of the aluminum slab was measured with a surface temperature guage to within $\pm 1^\circ\text{C}$.

Heat was lost from the sample upon transport to the rolls and

upon contact with the rolls. This effect was reduced and kept constant by treating all samples as much alike as possible and by rolling as quickly as possible and returning the sample to the oven.

At the end of the entire rolling and heating process, the samples were quenched in ice water to prevent further annealing.

B. DENSITY MEASUREMENTS

Density measurements were made with the aid of a density gradient column held at 23°C. The column was prepared from solutions of sodium bromide and water such that the density in the column ranged from 1.325 to 1.400 gm/cm³. Densities could be determined to within 0.0005 gm/cm³. Measurements were made 24 hours after the samples were placed in the column.

The following equation was used as an estimate of the volume percent crystallinity

$$X_c = \frac{(d_m - d_a)}{(d_c - d_a)} \times 100\% \quad (3B.1)$$

where X_c is the percent crystallinity, d_a is the amorphous density, d_c is the theoretical density of 100% crystalline regions, and d_m is the measured density of the sample. For PET, d_a is 1.333 gm/cm³ (32) and d_c is 1.455 gm/cm³ (14).

C. DIFFERENTIAL SCANNING CALORIMETRY

Experimental heats of fusion were determined as a function of roll reduction for Path I, II, and III using the Perkin-Elmer DSC-2. Three samples were run for each level of reduction for each of the three paths.

The instrument was calibrated each day with a tin sample (heat of fusion = 14.45 cal/gm; melting point = 231.88°C). The following conditions were used during calibration

Heating Rate	40°/min
Calorimeter Sensitivity	20 mcal/sec
Recorder Range	10
Chart Speed	80 mm/min
Temperature Range	438°K to 533°K

The same conditions except recorder range were used in the measurements on PET. A recorder range of 5 was used for PET samples in the temperature range of 320°K to 600°K.

Due to some confusion about the shape of the DSC curves at and around T_g , additional samples were run starting at lower temperatures, slower heating rates, and a more sensitive range. Using a dry ice and alcohol solution to cool the sample holders, the shape of the DSC curves could be determined in the temperature range of 290°K to 390°K.

Five to eight milligram sections of film seemed to be the optimum weight for obtaining good resolution and adequate peak areas.

When PET samples of low crystallinity are heated in the DSC, they crystallize further. This shows up as an exotherm on the DSC recorder. Since the newly crystallized material is eventually melted along with the crystalline material originally present in the sample, the area of the crystallization exotherm must be subtracted from the total peak area due to melting in order to obtain the correct value used in calculating

the original crystallinity. This will be called the corrected melting peak area.

For a given sample weight, the larger the corrected melting peak area, the higher the crystallinity.

With the more crystalline PET samples, two separate melting endotherms were sometimes observed. The areas of these endotherms were added together. This value was then used in the calculation of crystallinity.

To calibrate the peak areas, a tin standard was melted and the area of the endotherm measured. A standard heat of fusion per unit peak area was then calculated. The heat of fusion for the PET could then be calculated from equation 3C.1.

$$\text{Heat of Fusion} = \frac{\left(\begin{array}{c} \text{Corrected Melting} \\ \text{Peak Area} \\ \text{of Sample} \end{array} \right) \left(\begin{array}{c} \text{Heat of Fusion} \\ \text{per Unit Area} \end{array} \right) \left(\begin{array}{c} \text{Range Setting} \\ \text{for Sample} \end{array} \right)}{\left(\begin{array}{c} \text{Mass of} \\ \text{Sample} \end{array} \right) \left(\begin{array}{c} \text{Range Setting} \\ \text{for Standard} \end{array} \right)} \quad (3C.1)$$

The percent crystallinity was then estimated by the following equation.

$$\% \text{ Crystallinity} = \frac{\text{Heat of Fusion of Sample}}{\text{Heat of Fusion for 100\% Crystalline Sample}} \quad (3C.2)$$

The theoretical heat of fusion for 100% crystalline PET has been estimated by Wunderlich (86) to be 33.45 cal/gm and by Dole (18) to be 30.3 cal/gm. A value of 33.4±5 cal/gm was adopted for this research.

D. X-RAY ANALYSIS

To determine the optimum thickness for the highest diffracted intensity, the diffracted intensity was calculated for various thicknesses using equation 3D.1.

$$\frac{I}{I_0} = x \cdot e^{-(\mu/\rho) \cdot \rho \cdot x} \quad (3D.1)$$

where I_0 is the intensity of the incident beam, I is the intensity of the diffracted beam after passing through a thickness x , μ/ρ is the mass absorption coefficient, and ρ is the density. Values of μ/ρ are tabulated in various x-ray textbooks and in the International Tables for X-Ray Crystallography (49). Since PET is mostly carbon by weight, a good approximation of the relative diffracted intensity can be made using the mass absorption coefficient μ/ρ for carbon. A value of $4.2 \text{ cm}^2/\text{gm}$ corresponding to $\text{CuK}\alpha$ radiation was used (49). A density of 1.35 gm/cm^3 was used as a representative value for the PET samples.

Relative intensity values (I/I_0) were calculated and plotted as a function of thickness as shown in Figure 3D-1. The thickness at which the diffracted intensity is highest is about 1 mm.

WAXD Flat Plate Patterns

Wide angle x-ray diffraction (WAXD) patterns were made using a Philips Norelco x-ray generator and a flat plate camera. Sample to film distance was 3.91 cm. Patterns were obtained with the x-ray beam parallel to the RD, the TD, and the ND of the rolled film. Photographs were made for Paths I, II, and III as a function of roll reduction. Exposure times were typically one hour.

WAXD Pole Figures

Pole figures are a stereographic projection of the three dimensional distribution of the poles of a set of diffracting planes. This produces a two-dimensional representation of the pole distribution.

In the present study pole figures were made using a "single

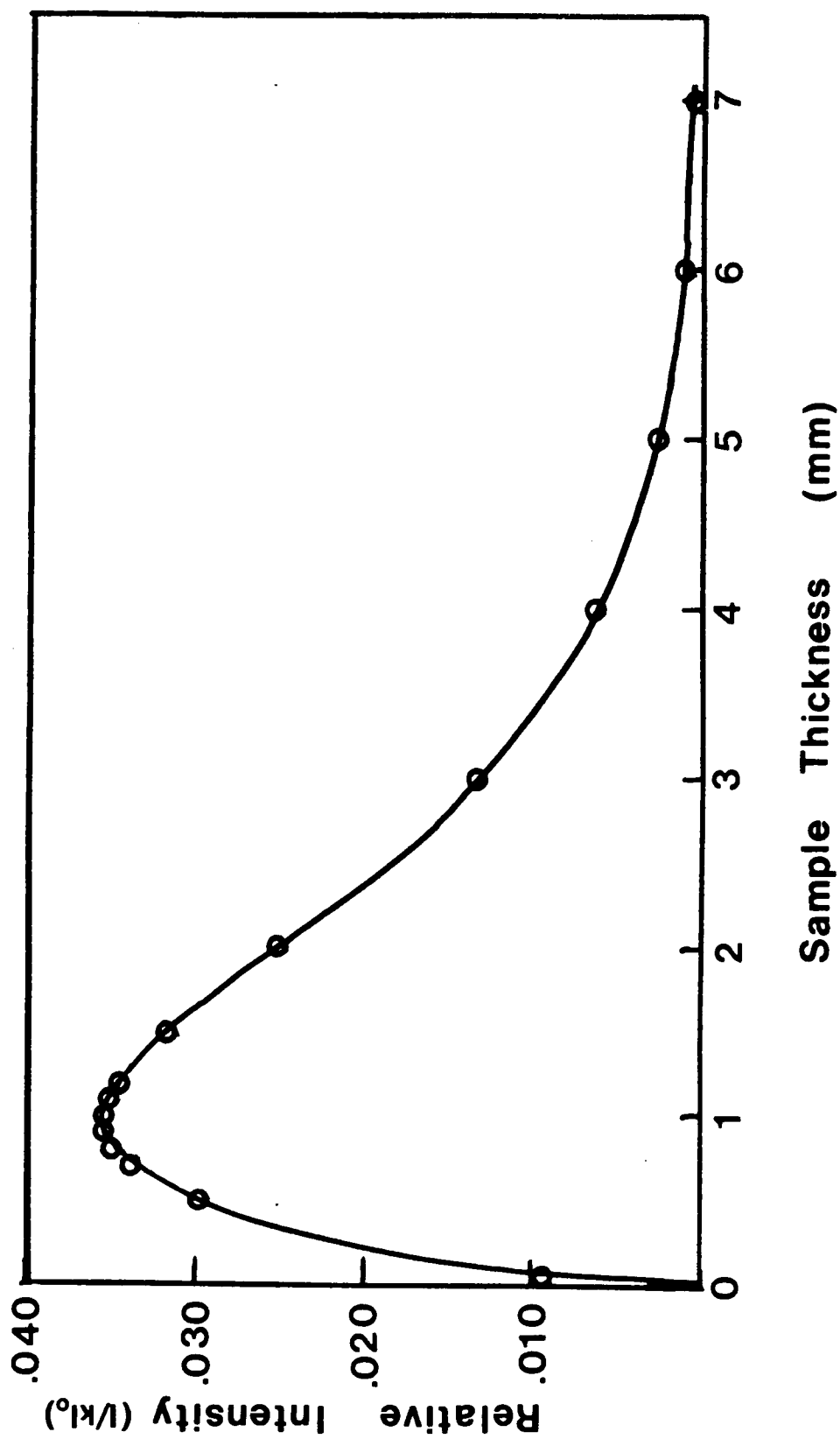


Figure 3D-1. Determination of optimum thickness for diffraction.

crystal orienter" (see Figure 3D-2). The movement of the orienter was controlled by, and intensity data recorded by, a PDP15 computer. (The pole figure apparatus had just been upgraded by Dr. Spruiell and Dr. Stansbury with the help of the electronics shop.)

Pole figures were made of the (100), (010), and ($\bar{1}05$) planes. The relation of these planes to the unit cell is shown in Figure 3D-3. The pole figures have as their reference axes the rolling thickness RD, the transverse direction TD, and the normal direction ND.

2 θ scans were performed to determine the proper 2 θ angle to record the intensity data for a given diffraction plane and to gather background intensity information (see Table 3D-1).

For the (100) and (010) planes, 2 θ scans were made from 35 $^{\circ}$ to 10 $^{\circ}$. Intensity levels were read at 35 $^{\circ}$ and 10 $^{\circ}$ and an appropriate interpolation was made to determine a background value. For instance, if the peak intensity for the (100) plane was at 2 θ = 25.75 $^{\circ}$, an intensity of 200 was recorded at 35 $^{\circ}$ and 500 at 10 $^{\circ}$, the calculation would be

$$\text{Background} = 500 - \left(\frac{15.75}{25} \right) \cdot 300 = 311$$

Background values were rounded to the nearest 5 counts.

Intensity readings for the construction of the pole figures were recorded at 5 $^{\circ}$ intervals from 0 $^{\circ}$ to 90 $^{\circ}$ in the radial direction, χ (in this case the samples were oriented such that χ is the angle between the ND of the film and the normal to the crystallographic planes which diffract at that χ angle). At each χ angle the sample is rotated 360 $^{\circ}$ in the circumferential direction ϕ and intensity readings taken at 10 $^{\circ}$ intervals.

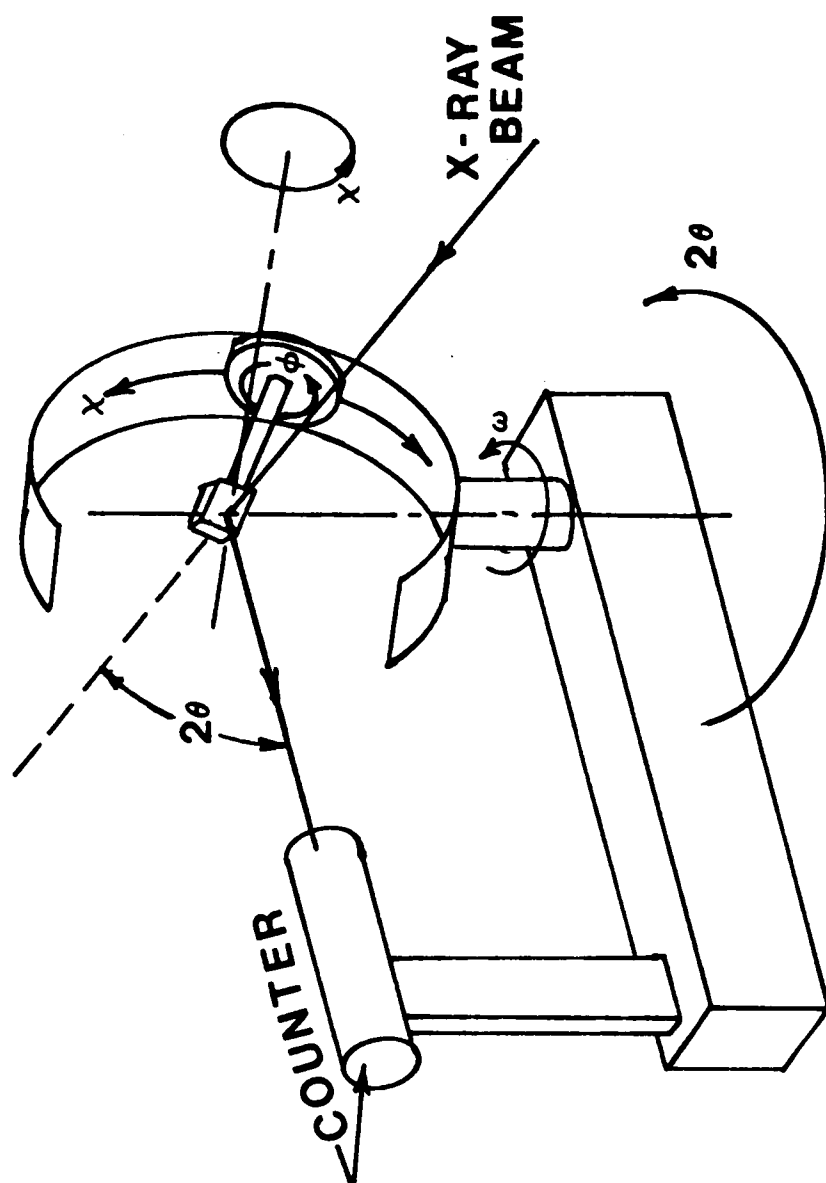


Figure 3D-2. Diagram of the single crystal orienter.

UNIT CELL OF PET

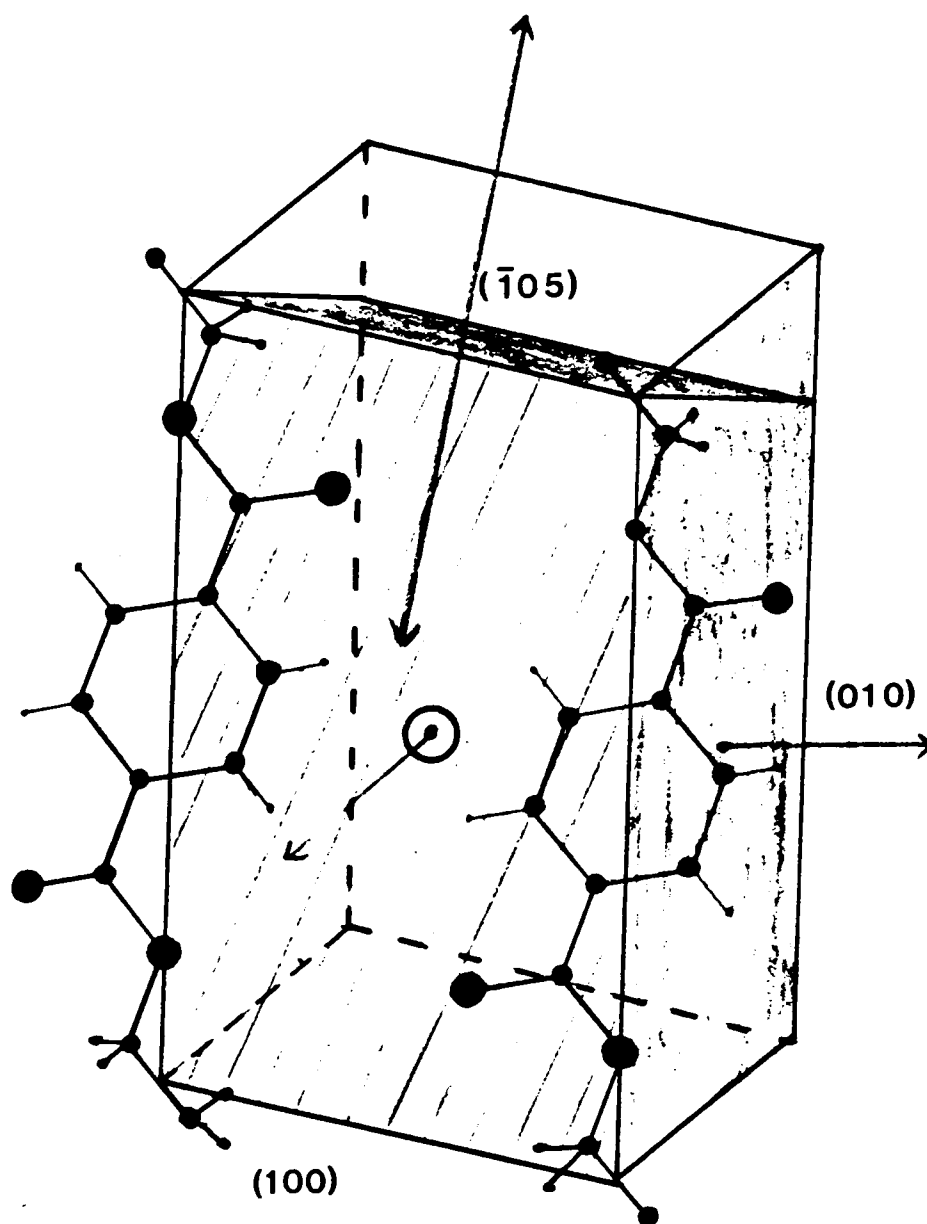


Figure 3D-3. Diagram of the unit cell of PET showing the (100), (010), and (105) planes.

TABLE 3D-1
DIFFRACTION ANGLES FOR CRYSTALLOGRAPHIC PLANES
USED IN POLE FIGURE ANALYSIS

Crystallographic Plane	Scanning Range	Approximate Peak Max
(010)	10° to 35°	17.5°
(100)	10° to 35°	25.5°
($\bar{1}05$)	35° to 50°	43.0°

In this manner intensity readings are taken over one hemisphere of the diffraction sphere.

Pole figures were plotted from the intensity-position data using an IBM 370 computer, a Tektronix plotter, and CALCOM plotting procedures.

In Path I samples the 2θ scans showed a broad peak from 2θ equal 13° to 27° with the maximum at about 21.5° . Pole figures were made at this 2θ angle for each reduction level. The poles are believed to be perpendicular to the chain axis.

In Paths II and III, pole figures were made for the (100), (010), and ($\bar{1}05$) crystalline planes as a function of roll reduction. The pole of the ($\bar{1}05$) plane lies at 9.8° to the c-axis and is a good measure of the chain axis orientation. The plane of the benzene rings is roughly parallel to the (100) plane, so the distribution of the (100) poles are a measure of the orientation of these rings. Both the (100) and (010) poles are perpendicular to the chain axis and their distribution gives additional information about the chain axis orientation.

The angles between intensity maxima and reference axes were measured by means of a Wulff net.

Orientation Factors

Herman's orientation functions were calculated using the $\overline{\cos^2 \chi}$ values obtained by using pole figure intensity data with RD as the reference axis. The overbar indicates that a spatial average has been taken.

Herman's orientation factor is related to $\overline{\cos^2 \chi}$ values by

$$f_c = \frac{\overline{3 \cdot \cos^2 \chi} - 1}{2} \quad (3D.2a)$$

where

$$\overline{\cos^2 \chi} = \frac{\int_0^\pi \int_0^{2\pi} I(\chi, \phi) \cdot \cos^2 \chi \cdot \sin \chi \cdot d\phi \, d\chi}{\int_0^\pi \int_0^{2\pi} I(\chi, \phi) \cdot \sin \chi \cdot d\phi \, d\chi} \quad (3D.2b)$$

White and Spruiell's biaxial orientation functions (82) were calculated using cosine square averages obtained for two different reference axes: the RD and the TD.

The biaxial orientation functions are defined in equations 3D.3 and 3D.4.

$$f_{cz}^B = 2 \cdot \overline{\cos^2 \chi_{cz}} + \overline{\cos^2 \chi_{cy}} - 1 \quad (3D.3)$$

$$f_{cy}^B = 2 \cdot \overline{\cos^2 \chi_{cy}} + \overline{\cos^2 \chi_{cz}} - 1 \quad (3D.4)$$

where $\overline{\cos^2 \chi_{cz}}$ is the mean square cosine of the angle between the c-axis and a reference axis ($y = TD, z = RD$). The orientation functions are then plotted on the triangle shown in Figure 3D-4.

SAXS Patterns

Small angle x-ray diffraction patterns were made on a Rigaku General Electric rotating anode x-ray generator. Air was evacuated from the camera since it will scatter a significant amount of radiation. Exposure times were typically 24 hours.

Diffraction patterns were made in the three mutually perpendicular directions of the sample as were the wide angle patterns.

The 2θ angles for the various diffraction patterns were

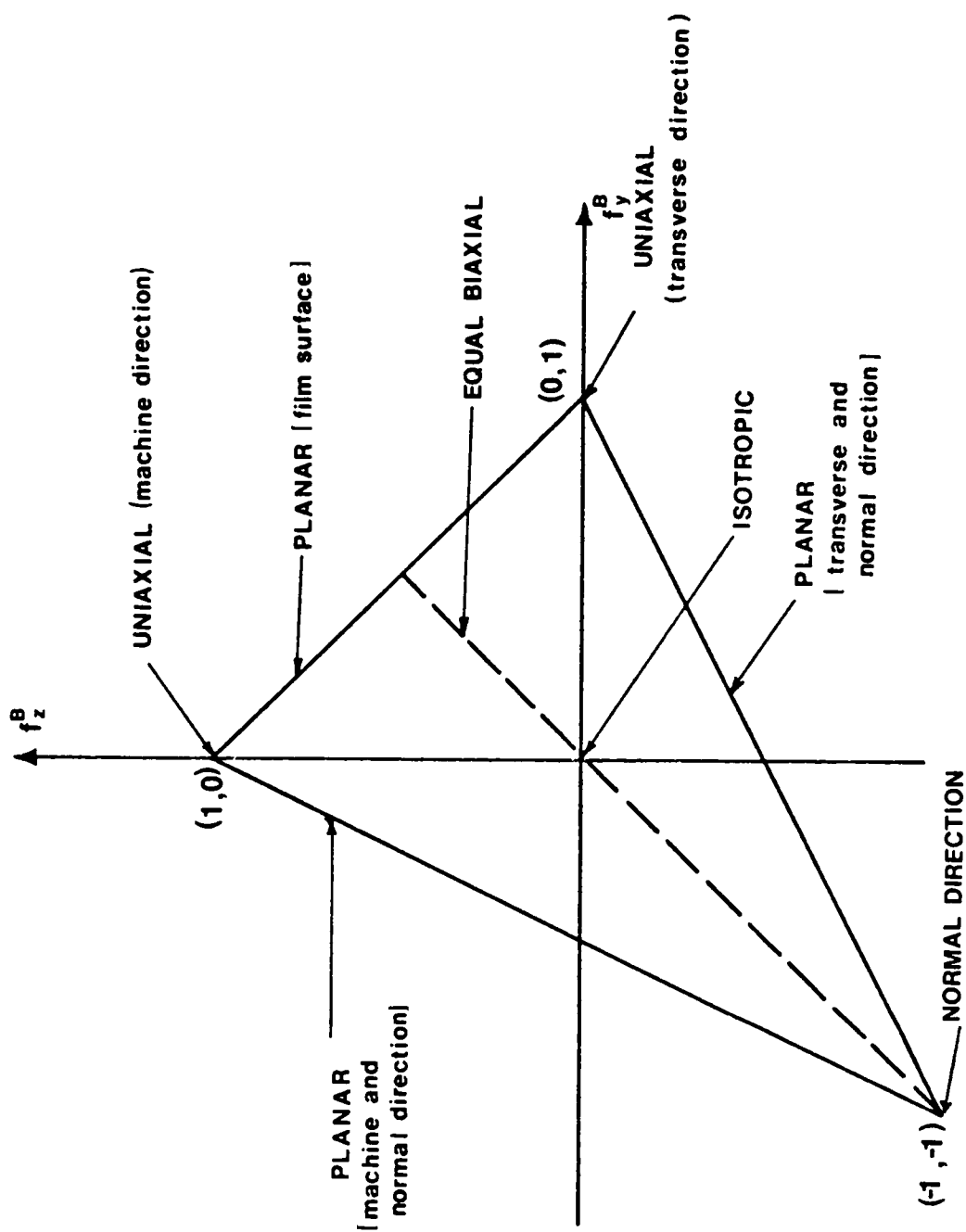


Figure 3D-4. White and Spruiell's biaxial orientation triangle.

Source: J. L. White and J. E. Spruiell, *Poly. Engr. Sci.*, **21**, 859-868 (1981).

calculated using equation 3D.5.

$$2\theta = \tan^{-1}\left(\frac{x}{2D}\right) \quad (3D.5)$$

where x is the distance between the diffraction spots and D is the sample to film distance (40.1 cm). The long period L could then be calculated using a form of Bragg's Law shown in equation 3D.6.

$$L = \frac{\lambda}{2 \cdot \sin \left[\frac{1}{2} \cdot \tan^{-1} \left(\frac{x}{2D} \right) \right]} \quad (3D.6)$$

where $\lambda = 1.542 \text{ \AA}$.

E. MECHANICAL TESTING

Tensile testing was performed on the rolled sheets produced in Paths I, II, and III. Dumbbell shaped samples (gauge length = 9.53 mm) were cut from the rolled sheets both in the RD and the TD. Tests were carried out at room temperature on a floor model Instron (Model TTD). The tests were performed according to ASTM procedure D638 type V. The elongation, however, was calculated from the distance the crosshead had moved at any given time during the test. The crosshead speed was 0.20"/min for a strain rate of about 50%/min.

Young's modulus, stress and strain at yield, stress and strain at break, and elongation to break were calculated from the force-time curves obtained.

The modulus E was measured from the slope of the initial portion of the curve.

The yield point was defined as a 2% plastic strain as shown in Figure 3E-1. This was necessary to prevent discrepancies caused by using

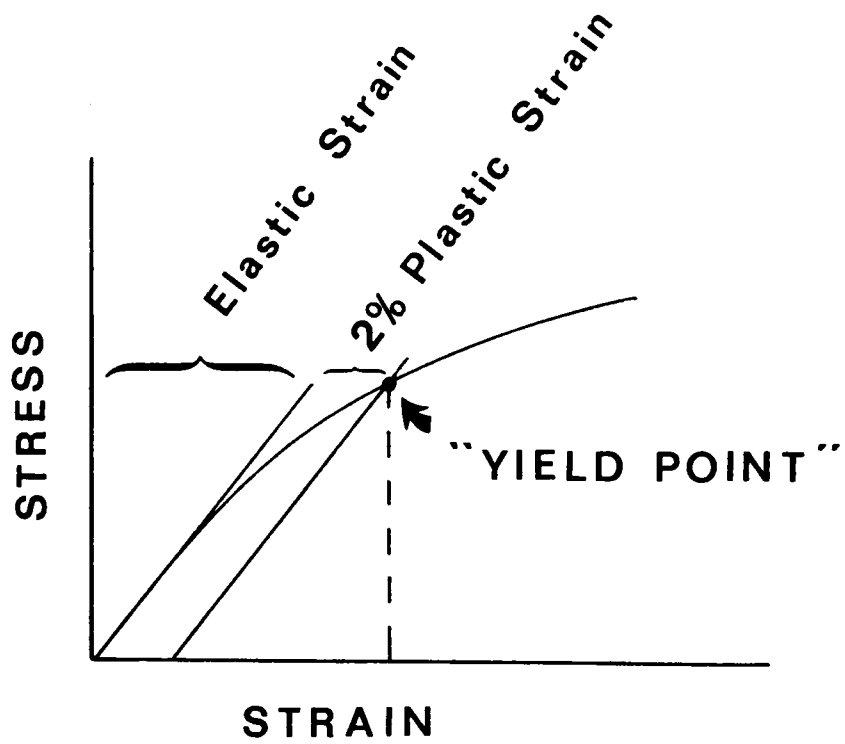


Figure 3E-1. Construction used to determine the yield point.

different definitions of the yield point in the various types of stress-strain curves encountered. This is a reasonable value since those samples which exhibited distinct yielding and necking showed a maximum stress at 2 to 3% plastic strain.

The tensile strength was taken to be the maximum load sustained by the samples divided by the original cross sectional area.

The equations used for the calculations of mechanical properties are presented in Appendix A.

CHAPTER IV

RESULTS AND DISCUSSION: PATH I, II, AND III

PET films were processed in four different ways as explained in Chapter III - Experimental Procedure. Samples were easily processed by Paths I and II. Path I samples were obtained by simply rolling amorphous sheets. Path II was a little more involved. First samples were annealed overnight at 150°C. Care was taken to make sure the samples remained perfectly flat during this time. Then these crystalline samples were rolled to the desired thicknesses. Path III was more difficult. First, samples were rolled just as for Path I. Then these samples were annealed at 150°C for about two hours. The difficult part was preventing shrinkage and keeping the samples flat enough to roll. Good samples were finally obtained for these three paths and a thorough investigation of their morphology and mechanical properties followed. Path IV, an attempt to roll and crystallize simultaneously, was less successful. Hence the bulk of the research concerns Paths I, II, and III. The results for these three paths are presented and discussed in this chapter. The meager results of Path IV are contained in a separate chapter.

A. DIMENSIONAL CHANGES

Changes Upon Rolling

For the first films that were rolled only changes in thickness were measured. After having done several of the initial experiments, it was noticed that in some cases the width of the film decreased at

high reductions. To investigate this effect a series of amorphous PET films were uniaxially rolled to various thicknesses. The width of the film remained almost constant down to $t/t_0 = 0.35$. At this point further reductions in thickness became difficult. The thickness remained essentially the same while the width decreased and the length increased. Reductions in thickness below about $t/t_0 = 0.30$ could not be achieved without shredding the film.

Crystalline samples were rolled and measured in the same manner. The dimensions of length and width as a function of thickness reduction are shown for both amorphous and crystalline samples in Figure 4A-1. The crystalline samples did not exhibit the reduction in width observed for the amorphous samples.

In the early experiments length and width changes were not recorded for the rolled samples, so all roll reductions are expressed as t/t_0 . In subsequent experiments, all roll reductions are expressed in terms of reduction in cross sectional area, A/A_0 (final cross sectional area divided by the initial cross sectional area). Table 4A-1 shows the A/A_0 and t/t_0 values obtained for each level of reduction in the three paths. In some cases, two pieces of film were rolled to the same approximate reduction so that enough material would be available for tensile testing in both the rolling direction and the transverse direction.

Dimensional Recovery Upon Free Annealing of Rolled Samples

Rollled amorphous samples were annealed without restraint in an air oven at 120°C . The shrinkage observed upon annealing is shown as a function of roll reduction (t/t_0) in Figure 4A-2.

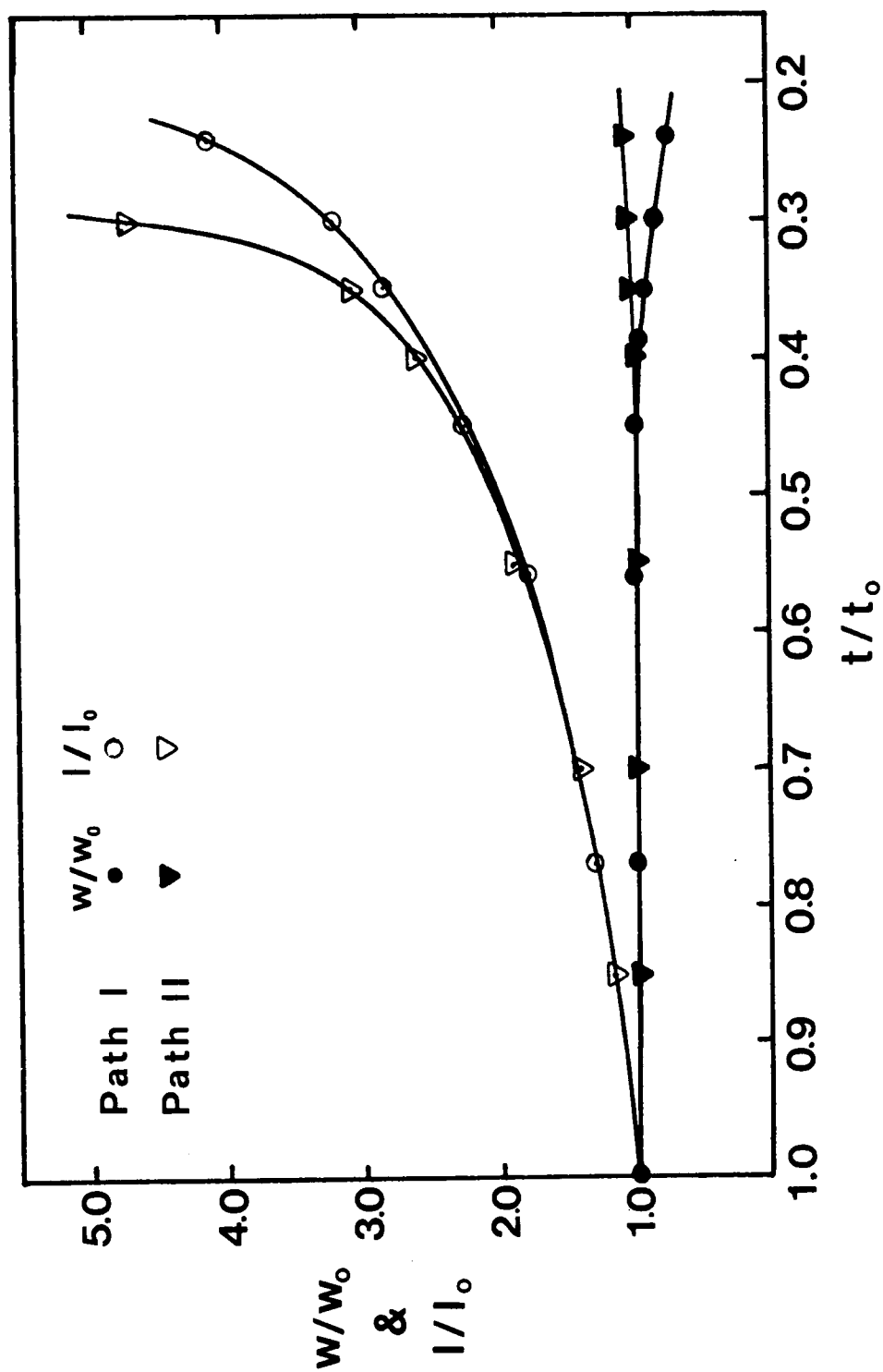


Figure 4A-1. Changes in width and length as a function of roll reduction for amorphous and crystalline samples.

TABLE 4A-1
ROLL REDUCTIONS OBTAINED FOR EACH FILM

I RD		I TD		II RD & TD		III RD		III TD	
t/t_o	A/A_o	t/t_o	A/A_o	t/t_o	A/A_o	t/t_o	A/A_o	t/t_o	A/A_o
1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
.77	.77	.77	.77	.86	.86	.75	.76	.75	.76
.56	.57	.56	.57	.70	.70	.57	.57	.57	.57
.45	.45	.45	.45	.55	.54	.46	.48	.45	.45
.40	.40	.39	.38	.40	.40	.38	.38	.41	.40
.35	.36	.38	.35	.35	.34	.36	.36	.38	.35
.30	.31	.34	.30	.30	.29	.29	.30	.34	.30
.24	.24	.32	.24	.28	.26	.24	.24	.32	.24

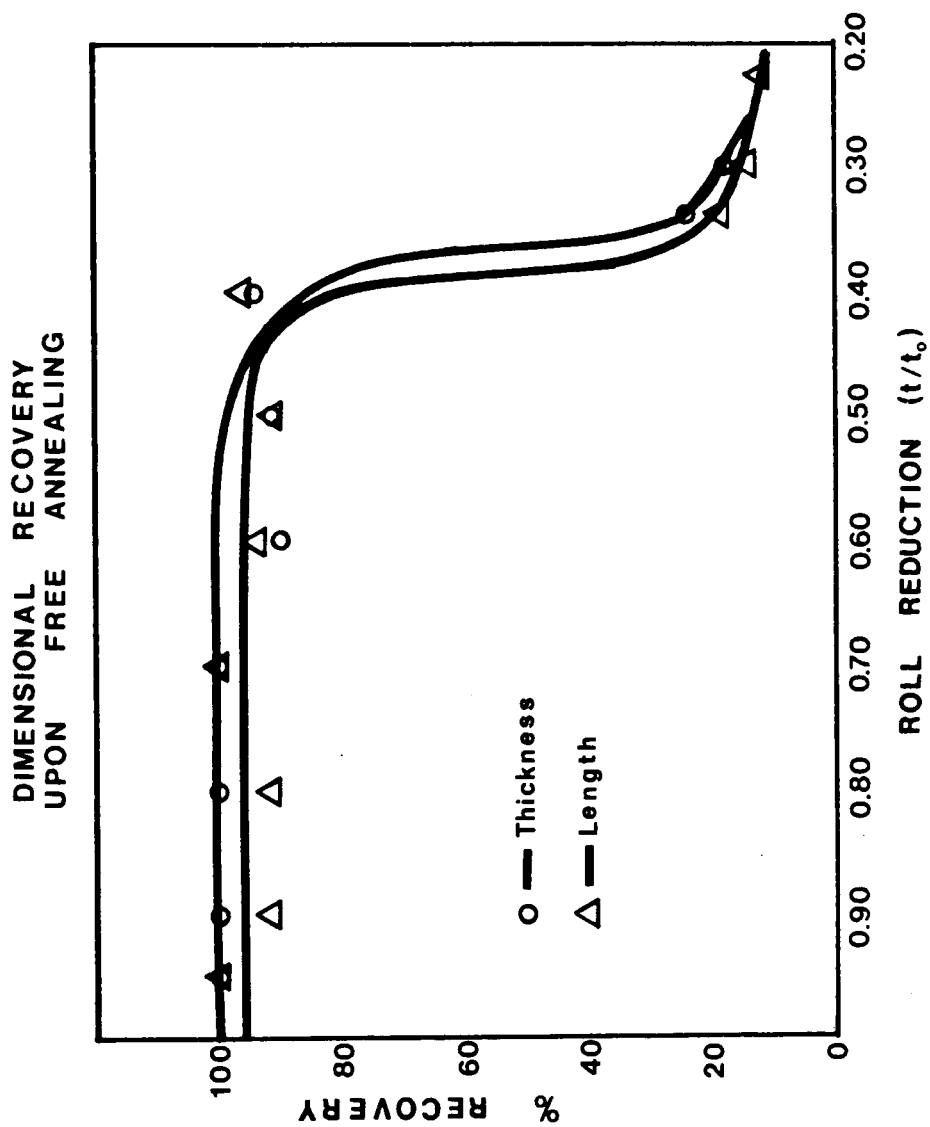


Figure 4A-2. Dimensional recovery of rolled amorphous samples upon free annealing at 120°C.

The dimensional recovery was calculated as follows.

$$\text{Percent Recovery} = \frac{\Delta x_A / b}{\Delta x_R / a} \times 100 \quad (4A.1)$$

where a is the dimension after rolling, b is the dimension before annealing, Δx_A is the change during annealing, and Δx_R is the change during rolling.

The rolled samples shrink almost back to their original dimensions before rolling, up to a roll reduction of t/t_0 of 0.40. At higher reductions the samples show much less recovery. This suggests that some strain induced crystallization may be occurring at the larger thickness reductions ($t/t_0 < 0.40$).

Maximum Reductions Obtained in One Pass

Some samples were rolled to determine the maximum reduction that could be obtained on the first pass through the rolls. A 45% reduction ($t/t_0 = 0.55$) in thickness could be easily obtained, but the samples tended to curl and become warm. Some cracks formed along the edges and a popping sound was heard.

As larger initial reductions were attempted, the samples became hotter and curled more extensively. Samples could be reduced about 50% in one pass without being destroyed. Beyond 50%, the samples made loud cracking sounds, curled upon themselves, and became very hot to the touch. These samples stiffened very quickly due to crystallization.

B. DSC AND DENSITY

General Features of the DSC Curves

1. Path I (Amorphous)

Representative DSC curves for Path I samples at various reductions are shown in Figure 4B-1. The most notable feature of the DSC curves is a large crystallization exotherm occurring anywhere from slightly above T_g to about 150°C depending on the amount of cold work. The greater the roll reduction, the closer to T_g the peak occurs. At high roll reductions, the crystallization peak area becomes smaller, while the melting peak area becomes larger. The transition temperatures, heat of crystallization, heat of fusion, and degree of crystallinity as a function of roll reduction are shown in Table 4B-1.

The melting peak appeared at about $250^{\circ}\text{--}260^{\circ}\text{C}$. The melting temperature seemed to be fairly independent of the amount of cold work performed.

The glass transition temperature at first dropped with rolling but then increased with high roll reduction.

2. Path II (Crystalline)

DSC curves for Path II samples are shown in Figure 4B-2. The curves for some samples show a relatively small melting peak between 160°C and 170°C . These peaks appear for samples with roll reductions between 1.0 and 0.55, growing smaller with higher reductions until they have disappeared at $A/A_0 = 0.40$. These peaks may be the result of imperfect crystallites melting.

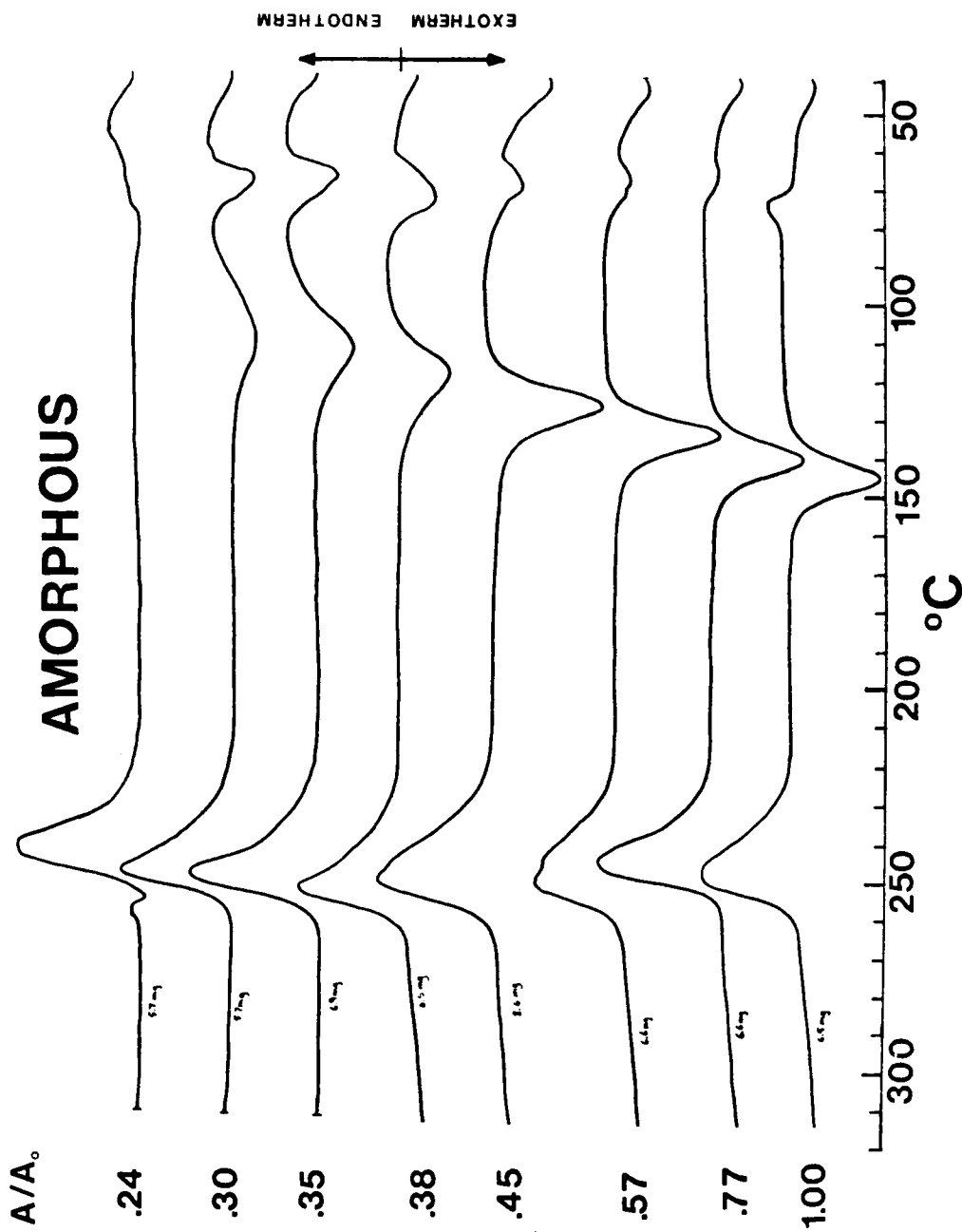


Figure 4B-1. DSC curves obtained for rolled amorphous (Path I) samples.

TABLE 4B-1
DSC RESULTS FOR PATH I SAMPLES

A/A ₀	T _g (°C)	Crystallization Exotherm		Melting Endotherm		Heat of Fusion - Heat of Crystallization (cal/gm)	Percent Crystallinity
		Peak Temp (°C)	Heat of Crystallization (cal/gm)	Peak Temp (°C)	Heat of Fusion (cal/gm)		
1.00	78	150	7.06	256	10.16	3.10	9.3
0.77	72	146	7.13	252	10.25	3.12	9.6
0.57	65	139	7.50	257	9.27	1.77	5.3
0.45	66	134	7.48	259	9.91	2.43	7.3
0.38	66	123	7.12	258	10.50	3.38	10.7
0.35	74	120	7.11	260	11.53	4.42	13.5
0.30	75	117	6.98	258	12.18	5.20	16.0
0.24	75	1	1	252	13.15	13.15 ¹	39 ¹

¹Crystallization exotherm superimposed on T_g. Hence % crystallinity may be artificially high.

CRYSTALLINE

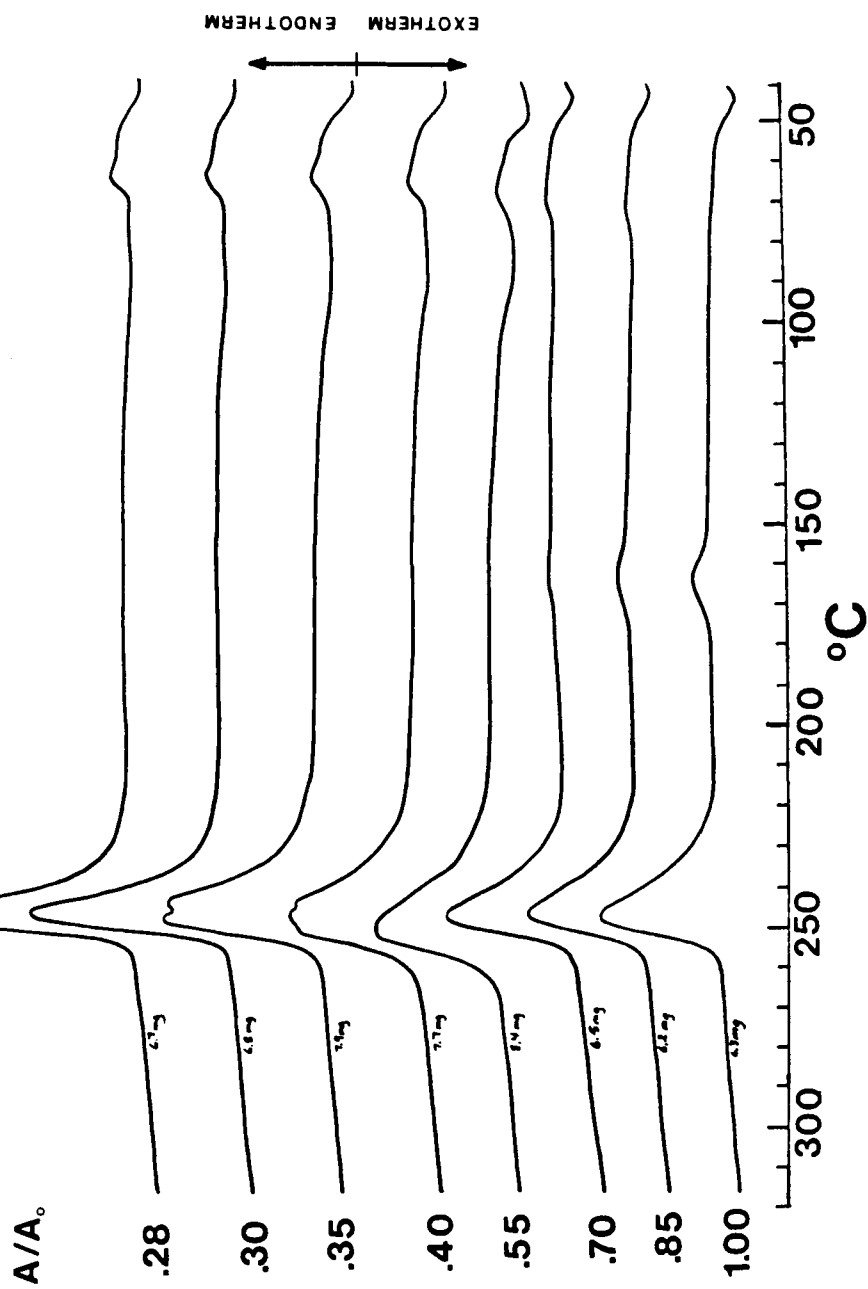


Figure 4B-2. DSC curves obtained for rolled crystalline (Path II) samples.

The main melting peak occurred at about 230°C - 260°C , with the maximums occurring at about 245°C . The peaks gradually changed from a broad and short shape at low reductions to a narrower and taller shape at higher reductions. This may indicate the average crystallite size is becoming more uniform. The crystallites may start out with various sizes but as they are rolled they all become crushed into a smaller more uniform size.

3. Path III (Rolled and Annealed)

The DSC curves for this path (see Figure 4B-3) show a relatively small endotherm at about 160°C - 170°C at all reduction levels. These may be due to melting of imperfect crystallites or paracrystalline regions. The temperature at which the peak occurred did not seem to be too sensitive to the amount of cold work performed. The weight normalized area of the peak dropped off sharply at high reductions ($A/A_0 < 0.32$). A change in heat capacity was noted in the region of the peak for the highly rolled samples.

The larger endotherm, representing the heat of fusion, occurred over the range of 225°C - 260°C . The "melting temperature" and the temperature at the peak maximum appeared to be largely independent of roll reduction, occurring at about 225°C and 250°C respectively for all samples. The shape of the peak, however, tended to become more narrow with increasing roll reductions as in the initially crystalline PET samples.

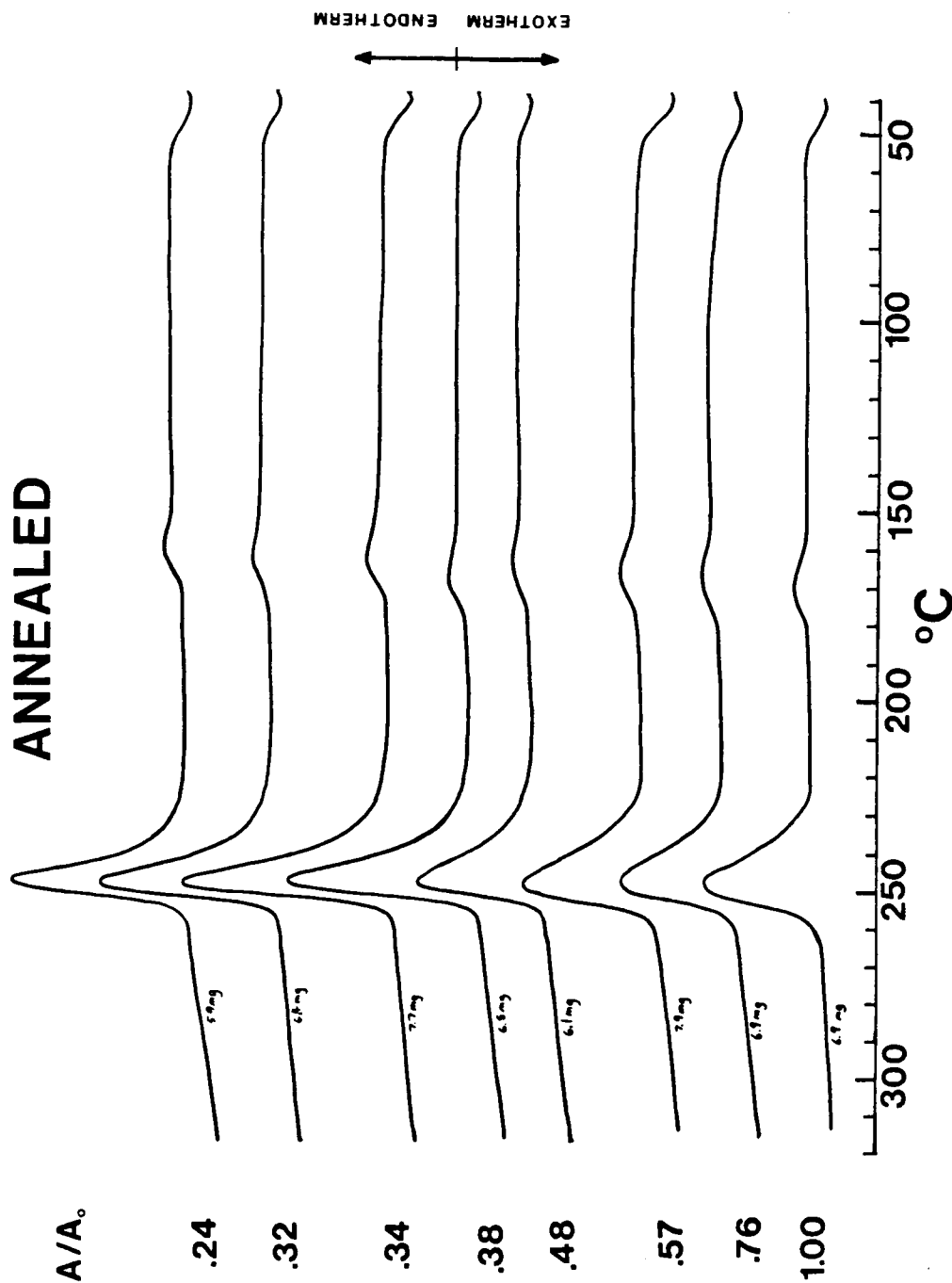


Figure 4B-3. DSC curves obtained for rolled and annealed (Path III) samples.

Determination of Crystallinity

Both density and heat of fusion measurements were made in an attempt to determine the crystallinity of the rolled film. Figure 4B-4 shows the density as a function of roll reduction for the different paths, while Figure 4B-5 shows the crystallinities calculated from the heats of fusion as a function of roll reduction.

1. Path I (Amorphous)

For the initially amorphous films the density increases with rolling. According to equation 3B.1 (page 68), this indicates an increase in crystallinity. The corresponding crystallinity computed from equation 3B.1 is shown on the right side of Figure 4B-4.

The crystallinity, as calculated from heats of fusion of the rolled amorphous samples, generally increases with rolling especially at the higher reductions (see Figure 4B-5).

Both methods indicate an increase in crystallinity with increasing roll reductions, but the actual crystallinity values obtained from the DSC measurements tend to lie above those obtained from density measurements.

2. Path II (Crystalline)

For the samples which were highly crystalline before rolling, the DSC data shows an initial slight decrease in crystallinity down to an A/A_0 of about 0.55, but at higher roll reductions the crystallinity increases with rolling, reaching a final value slightly higher than that of the unrolled samples (see Figure 4B-5). The density, however, decreases almost linearly with increasing roll reductions (see Figure 4B-4).

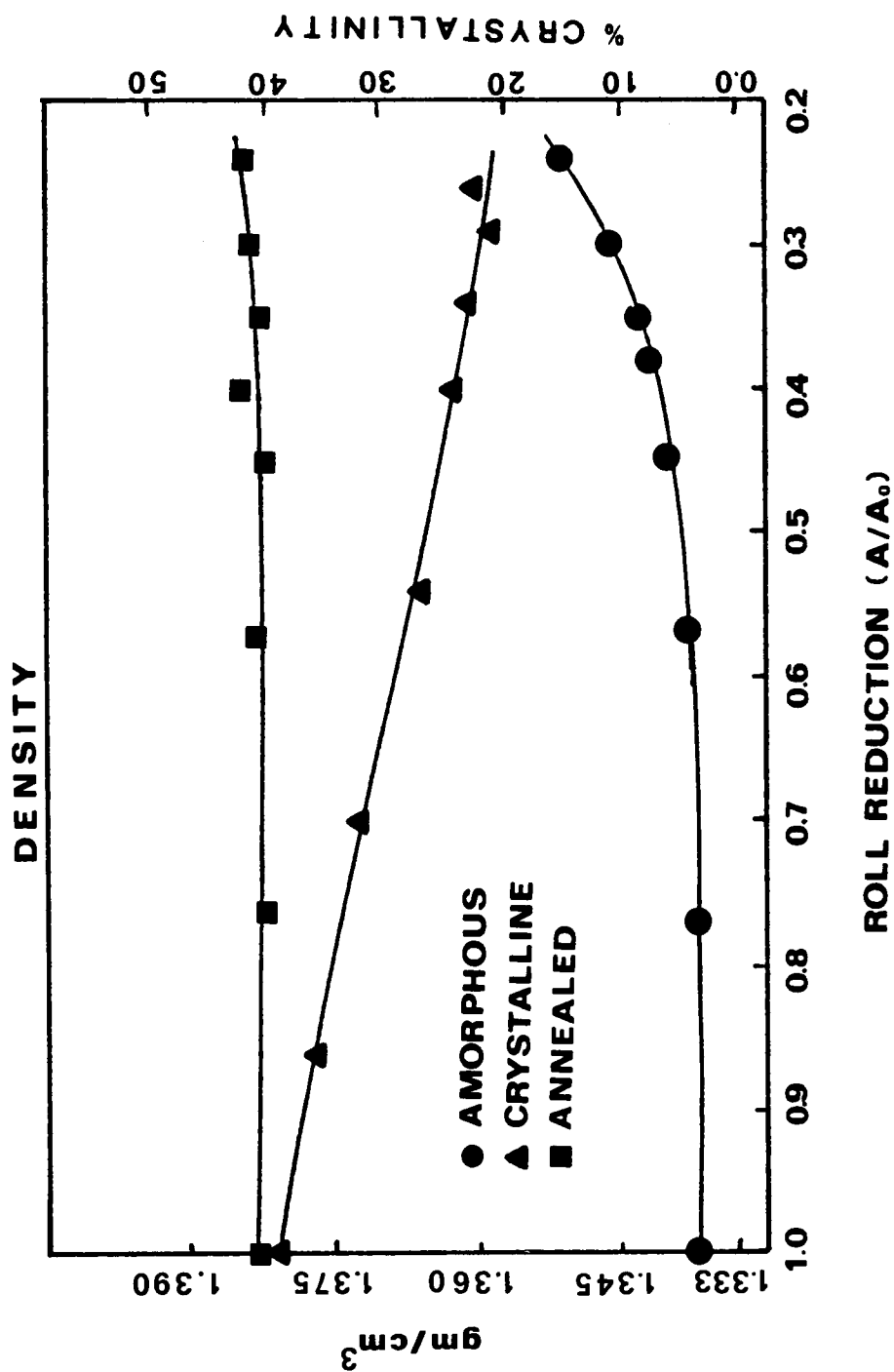


Figure 4B-4. Density as a function of roll reduction for Paths I, II, and III.

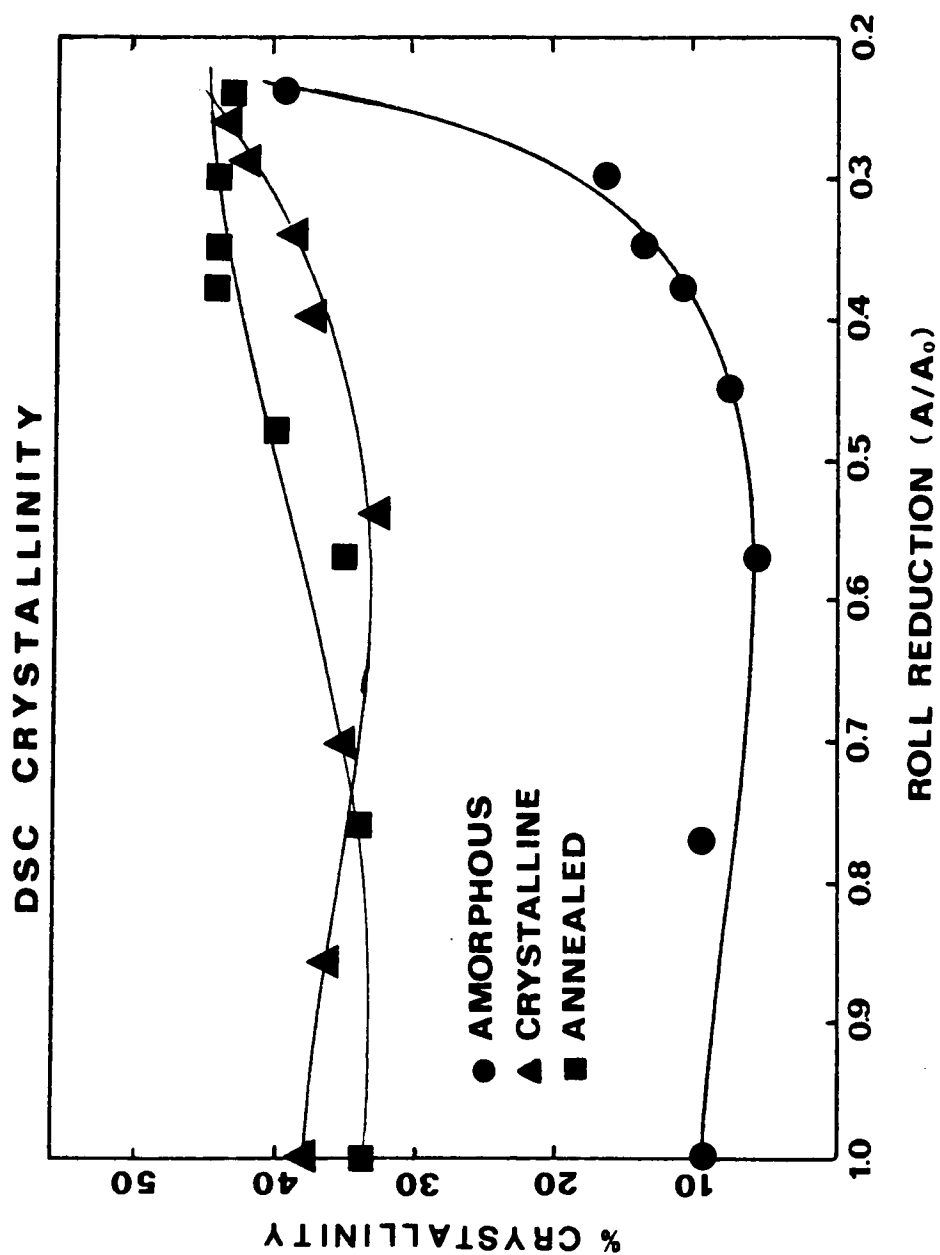


Figure 4B-5. Crystallinities calculated from heat of fusion data. The crystallinity for Path I at $A/A_0 = 0.24$ is probably overestimated due to experimental problems.

3. Path III (Rolled and Annealed)

Density measurements indicate about a 2% increase in crystallinity over the range of reductions, while DSC measurements indicate about a 10% increase.

The percent crystallinity calculated from density measurements is about 42% at the highest roll reduction. Calculations from DSC data indicate about 34% crystallinity in the unrolled sample increasing to about 44% in the highly rolled samples (see Figures 4B-4 and 4B-5).

Discussion of DSC and Density Results

1. Path I (Amorphous)

The DSC curves show that as the roll reduction increased, the temperature at which the samples crystallize and the amount of crystallization occurring during the scan both decrease. This indicates that the strain present in the rolled samples reduces the thermal energy needed for crystallization. The more strain present in the sample, the closer to T_g crystallization can occur. Since the crystallization peak grows smaller with rolling, some crystallization must occur during rolling, leaving less material to crystallize during the DSC scan. Crystallinities calculated from both density and heat of fusion results indicate a small rise in crystallinity during rolling.

2. Path II (Crystalline)

The DSC curves show two melting peaks at low reductions: a relatively small endotherm at about 160⁰-170⁰C and a larger peak from about 230⁰-260⁰C. The first peak is probably due to the melting of

imperfect crystallites, while the larger endotherm is due to melting of highly crystalline material.

As roll reductions increase, the broad short melting peak becomes narrower and taller. This indicates the crystallites become more uniform in size. That is, the crystallites may be of various shapes and sizes at low reductions but during rolling they are crushed into a smaller more uniform size. The melting temperature, however, does not change significantly.

The density decreases during rolling from 1.381 to 1.360 gm/cm³ while DSC results indicate an increase in crystallinity from about 40% to 43%. Apparently the crystallites are crushed during rolling and some voids are formed. The density of the solid material was calculated from the percent crystallinity obtained from the heat of fusion data. The void fraction was then estimated from

$$\text{Percent Voids by Volume} = \frac{\bar{V}_F - \bar{V}_D}{\bar{V}_D} \quad (4B.1)$$

where $\bar{V}_F$ is the specific volume of solid material calculated using heat of fusion data and $\bar{V}_D$ is the specific volume of bulk rolled samples as obtained from density gradient column data. Figure 4B-6 shows the void fraction increasing with increasing roll reduction.

3. Path III (Rolled and Annealed)

The DSC curves for this path showed a small endotherm at about 160°-170°C in addition to the larger melting peak from 225°-260°C. These may be due to melting of imperfect crystallites or paracrystalline material.

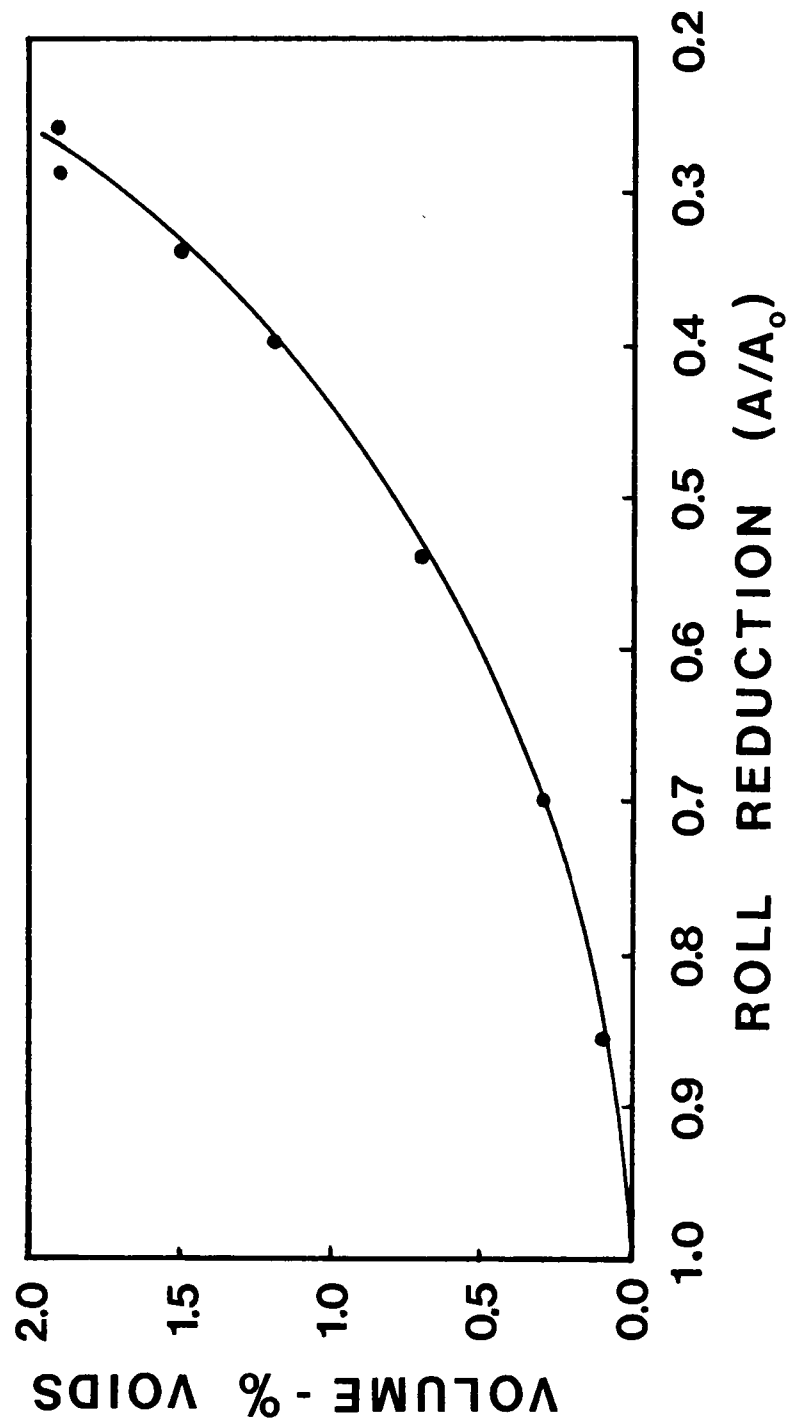


Figure 4B-6. Volume fraction of voids in Path II samples as a function of roll reduction.

The shape of the melting peak again becomes narrower with increasing roll reductions. One explanation would be that the crystallites are becoming more uniform in size and thus tend to melt more nearly at the same temperature.

Density measurements indicate a very slight increase in crystallinity over the range of reductions, while DSC measurements indicate about a 10% increase. Hence, highly rolled material crystallizes to a higher degree during annealing than unrolled or moderately rolled material. This is in good agreement with other work on deformed PET which shows that strained samples crystallize more rapidly than unstrained samples during annealing and reach a higher ultimate degree of crystallinity (71, 77).

C. WAXD

Flat Plate Patterns

A series of film patterns were taken with the incident beam parallel to each of three mutually perpendicular axes (RD, TD, & ND) of the samples for each of the different processing paths. These patterns provide qualitative information about the changes in chain orientation and crystallinity as a function of roll reduction.

1. Path I (Amorphous)

Figure 4C-1 shows the WAXD patterns obtained for rolled amorphous PET. The patterns show very broad diffuse peaks. There is an azimuthal variation in intensity which indicates that some sort of orientation occurs during rolling. The diffuse peaks observed for these samples

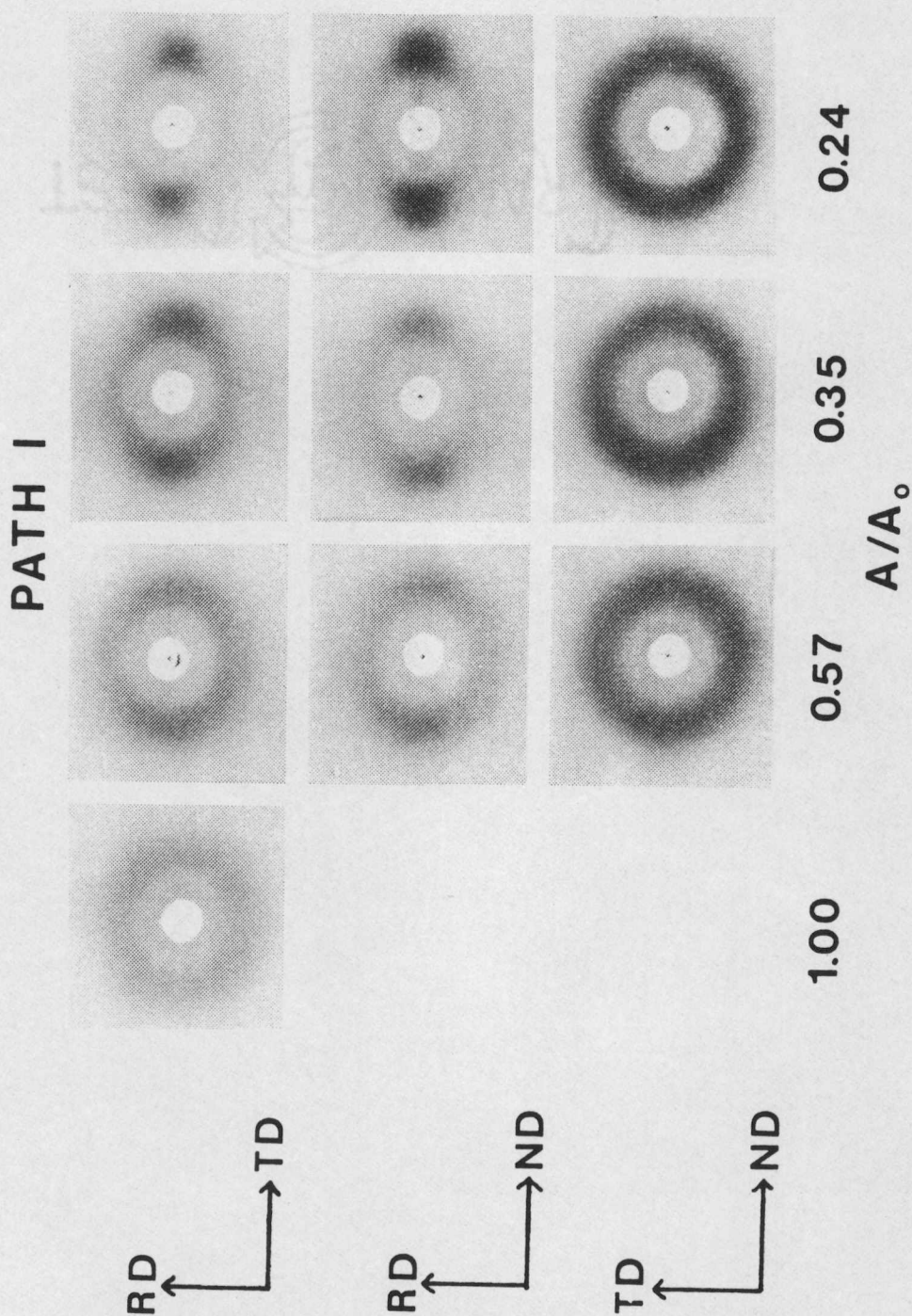


Figure 4C-1. WAXD patterns for Path I samples. Patterns were taken with the beam parallel to ND, TD, and RD.

are perhaps best explained in terms of a transformation from the initial amorphous structure to a somewhat more ordered paracrystalline structure which increases in degree of order with increases in roll reduction. At high roll reductions there is evidence that small crystallites have formed. The existence of the paracrystalline structure is reasonable since both DSC and density measurements indicate some degree of crystallinity in the rolled samples.

One can reason that the broadening due to paracrystalline disorder can be so great that diffraction from the precursors of the $(hk0)$ planes will appear as a single broad peak in a 2θ scan rather than as several distinct peaks. The intense inner ring observed for unrolled samples spans from 2θ angles around 13° to about 25° with the maximum at about 21.5° . In crystalline PET, the most intense $hk0$ reflections are from the (100) , $(1\bar{1}0)$, and the (010) planes. These reflections occur at 2θ angles of about 25.8° , 23° and 17.3° , respectively. The $(1\bar{1}0)$ and (010) peaks fall within the range of the broad observed peak. It seems reasonable, then, that the observed diffraction in unrolled and lightly rolled samples is due to some interchain distance and is roughly equivalent to highly broadened and overlapping $(1\bar{1}0)$ and (010) peaks.

In the highly rolled case ($A/A_0 = 0.24$) the intensity is concentrated along the equator and extends from $2\theta = 14^\circ$ to $2\theta = 27^\circ$. This suggests the chains have aligned and moved closer together. For a crystalline sample the diffraction from (100) planes ($2\theta = 25.8^\circ$) would now lie within this range.

Another very weak ring of arc is observed in most samples at a peak 2θ angle of about 40 to 41° . This interference may be due to some

repeat distance along the chain, perhaps the same repeat distance from which the ($\bar{1}05$) plane arises in crystalline PET.

In the unoriented sample the diffraction rings exhibit no azimuthal variation of intensity, indicating no preferred orientation of the chains. As the samples are rolled the intensity of the inner ring increases at the equator in patterns taken with the x-ray beam parallel to ND or TD. These changes indicate that the chains become aligned in the rolling direction during rolling.

At the highest reduction the diffraction patterns become better defined. In addition to the intensity concentrated at the equator, there is a ring at 14° , a peak along the meridian at about 25.9° , and a broad arc peaking along the meridian at about 41° . The presence of some discrete scattering at the higher reductions would seem indicative of the formation of small crystallites. These changes correlate well with the increase in density and heat of fusion with increased reduction by rolling.

The x-ray patterns obtained with the beam parallel to RD show little or no variation in intensity around the circumference of the ring at any roll reduction.

At first glance, one would assume the orientation is random about the RD, but work done with pole figures indicates otherwise. Those results will be given in a separate section.

2. Path II (Crystalline)

Figure 4C-2 shows a progression of WAXD patterns taken of rolled crystalline PET as a function of roll reduction. Several

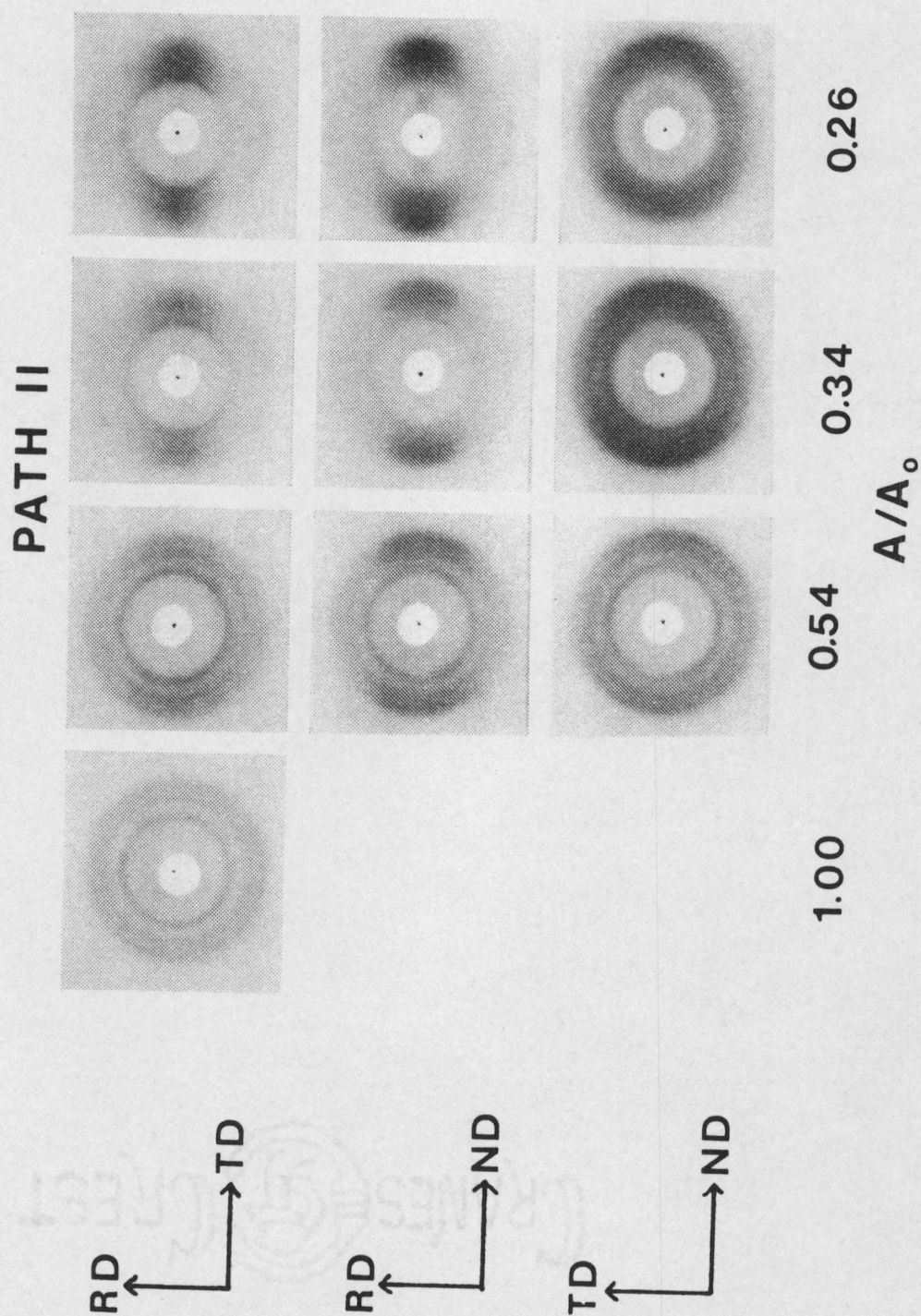


Figure 4C-2. WAXD patterns for Path II samples.

distinct Debye rings can be seen in the unrolled case. The most intense rings were indexed as reflections from (010), (1 $\bar{1}$ 0), and (100) crystalline planes (from lowest to highest 2θ values). In the unrolled case, constant intensity around the Debye ring is observed, indicating no preferred orientation. As the polymer is rolled, these rings sharpen into arcs. Appreciable line broadening occurs as the roll reduction increases.

The line broadening is probably due to a distribution of d-spacing caused by strain and perhaps to decreasing crystallite size. It seems likely that as the samples are rolled, the crystallites are fragmented and their unit cells are somewhat distorted.

A preferred orientation of rings can be detected even in the patterns taken with the beam parallel to RD. Hence, the orientation here is not a simple uniaxial type but a more complex biaxial type. More data in the form of pole figures is necessary to accurately describe the orientation. These will be shown in another section.

3. Path III (Rolled and Annealed)

Figure 4C-3 shows the series of WAXD patterns taken of the fixed annealed samples. Five distinct Debye rings can easily be seen in the pattern from the unrolled sample. A constant intensity is observed around the ring. As the samples are rolled the rings gradually become well defined arcs. No line broadening is apparent.

At the highest roll reduction ($A/A_0 = 0.24$), the pattern taken with the beam parallel to ND is similar to that of a highly oriented fiber. Diffraction from as many as 11 different crystalline planes can

PATH III

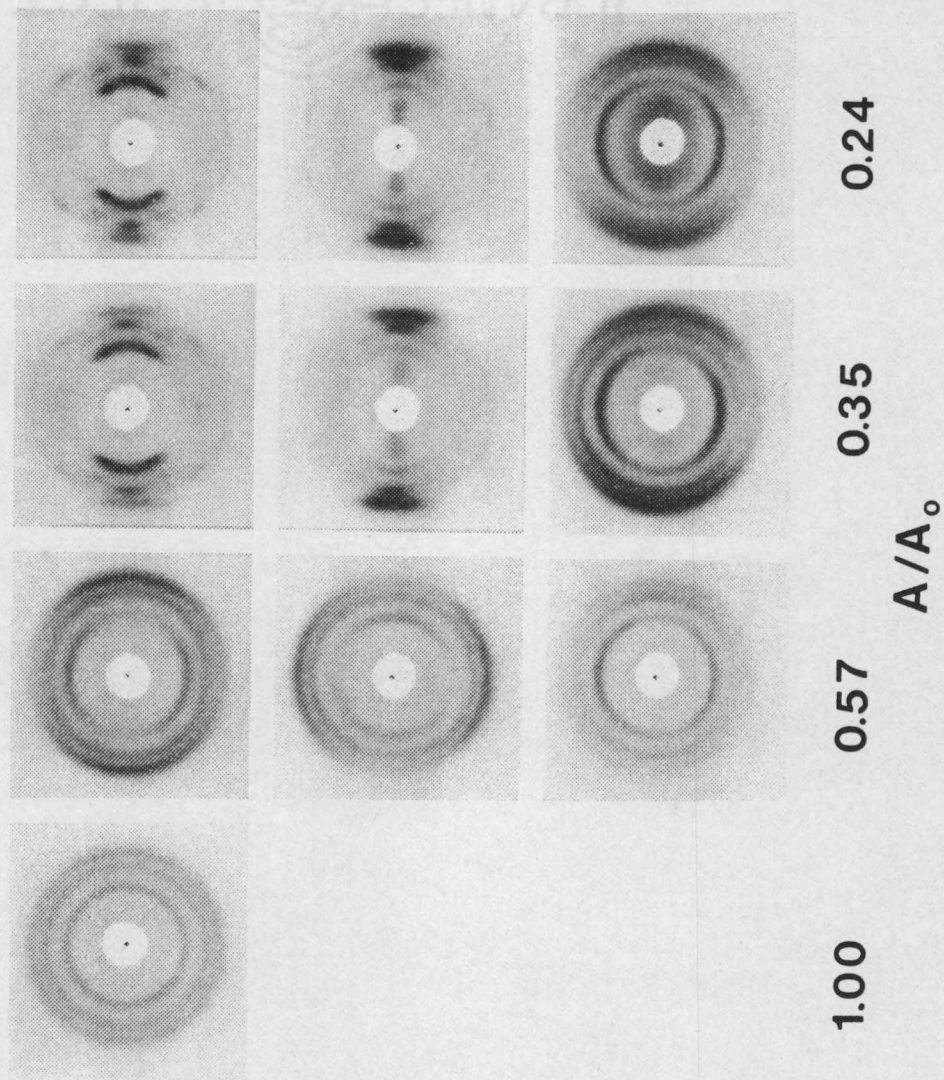


Figure 4C-3. WAXD patterns for Path III samples.

be detected. The d-spacings were calculated and determined to be the same as those reported by Bosely (8).

In contrast to fibers, however, patterns taken with the beam parallel to RD show preferred orientation. Hence, the morphology is not of the simple uniaxial type and pole figures will be used to further define the orientation of the unit cells.

Pole Figures

In order to gain more quantitative information than the WAXD flat plate patterns afford, pole figures were prepared. The pole figure shows the intensity of the selected diffraction peak at all orientations of the sample in space with respect to the x-ray beam. The intensity data is quantitative and may be plotted in the form of contour lines of equal intensity. Thus, much information can be gained about the distribution and orientation of crystallographic planes and chain axes.

1. Path I (Amorphous)

Samples prepared by rolling amorphous films have low crystallinity (<15% according to density measurements). The WAXD patterns did exhibit diffuse halos which seemed to indicate some sort of preferred orientation of the chains. A 2θ diffractometer scan did not show distinct crystallographic diffraction peaks but, instead, a broad peak ranging from $2\theta = 13^\circ$ to $2\theta = 27^\circ$. The peak maximum was at 21.5° . Pole figures were made at this 2θ angle for each Path I sample. This measurement is believed to determine the distribution of normals to a hypothetical set of planes in the paracrystalline structure which are parallel to the chain axes. The orientation of these hypothetical planes give

information about the chain orientation in the same manner as do the $hk0$ reflections from crystals. To a first approximation, the structure can be considered as hexagonally packed chains. For such a hexagonally packed structure the peak at 21.5° (2θ) could be thought of as the 100 reflection.

The pole figures for Path I samples are shown in Figure 4C-4. The numbers on the contours give the intensity in "times random" units.

In the unrolled sample, there is little variation in intensity indicating no preferred orientation of the chains. At $A/A_0 = 0.57$, some variation in intensity is shown. The contour lines are beginning to show a concentration of poles near the equator. There is also a slight tendency for concentration near the normal direction, ND. At $A/A_0 = 0.38$, there is much more variation in intensity, the maximum intensity being centered about the normal direction, ND. At $A/A_0 = 0.35$, the intensity at the equator has increased again at the expense of the other regions. The contour lines are closer together and run nearly parallel to the equator. The maximum noted at the ND is slightly stronger. At the highest reduction ($A/A_0 = 0.24$) the intensity sharpens further about the equator and the intensity at the ND increases further.

2. Path II (Crystalline)

For Path II (and III) samples, pole figures were made of the (100), (010), and ($\bar{1}05$) crystallographic planes. The (100) and (010) poles are perpendicular to the chain axes and these pole figures help to provide information on the orientation of the chains within the sample. Since the benzene rings in the chains are almost coplanar with

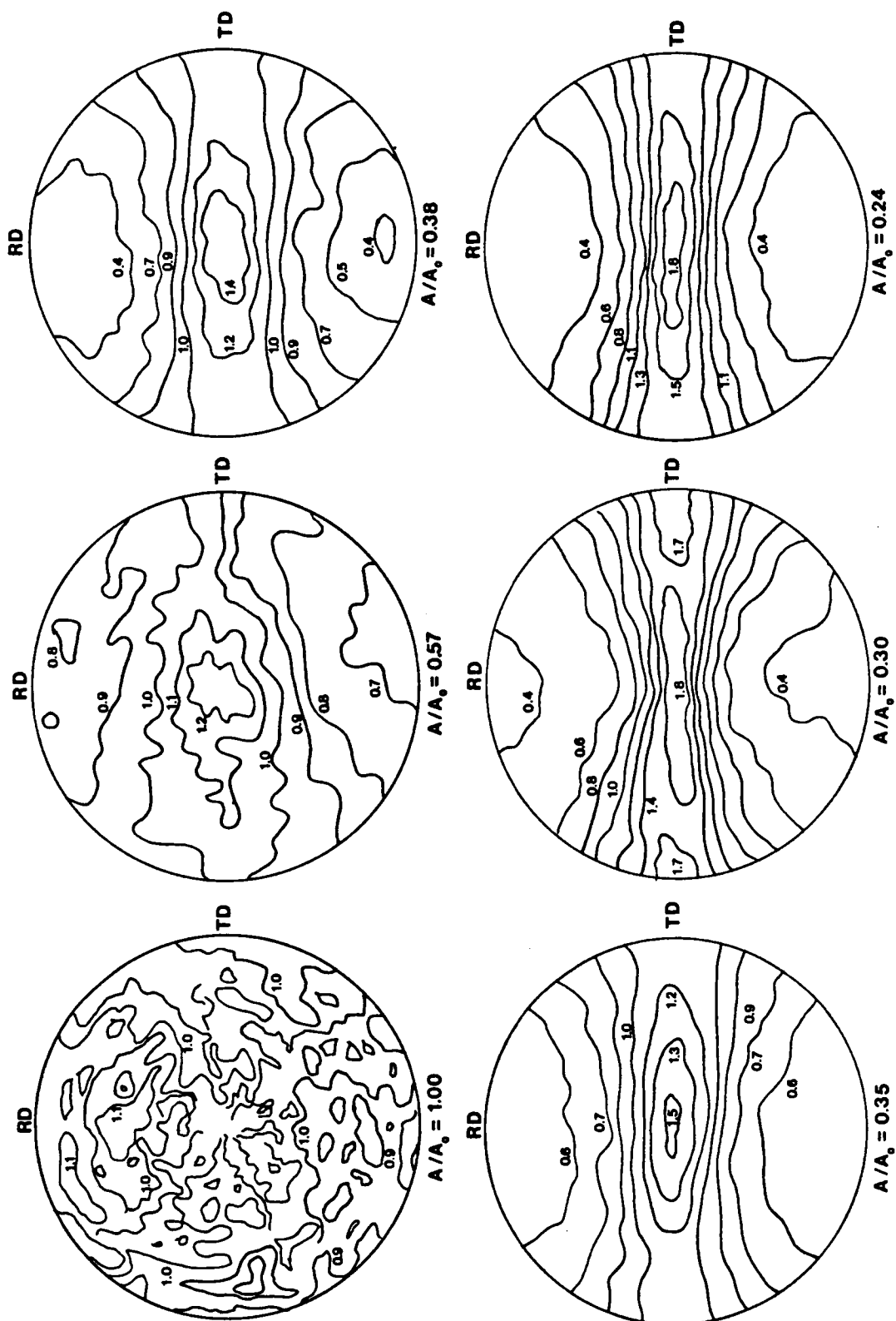


Figure 4C-4. Pole figures of Path I samples taken at $2\theta = 21.50^\circ$.

the (100) plane, the (100) pole figures tell something about the spacial distribution of these rings in the sample. The ($\bar{1}05$) pole is almost parallel to the chain axis and gives direct information about the chain orientation.

Figure 4C-5 shows the (100) pole figures as a function of roll reduction. The pole figures indicate the (100) planes become aligned parallel to RD during rolling, with the preferred orientation being parallel to the plane of the film. In other words, the benzene rings become preferentially oriented in the plane of the film during rolling.

The (010) pole figures (see Figure 4C-6) also show a tendency of the (010) planes to orient parallel to the RD during rolling, but to a lesser extent than the (100) planes. At the higher reductions, intensity maxima are noted along the equator at about 15° from the transverse direction.

The ($\bar{1}05$) pole figures (see Figure 4C-7) show that preferred orientation of the chains approximately parallel to the RD develops gradually with increasing rolling reductions. At high reductions, strong maxima are noted about the RD in the pole figures. This indicates the chains become preferentially oriented in the RD at high reductions, the degree of orientation increasing with increasing reduction.

3. Path III (Rolled and Annealed)

Pole figures were made of the (100), (010), and ($\bar{1}05$) crystallographic planes for Path III samples just as they were for Path II. The high crystallinity and crystallite perfection of these annealed samples allowed sharp, intense pole figures to be made.

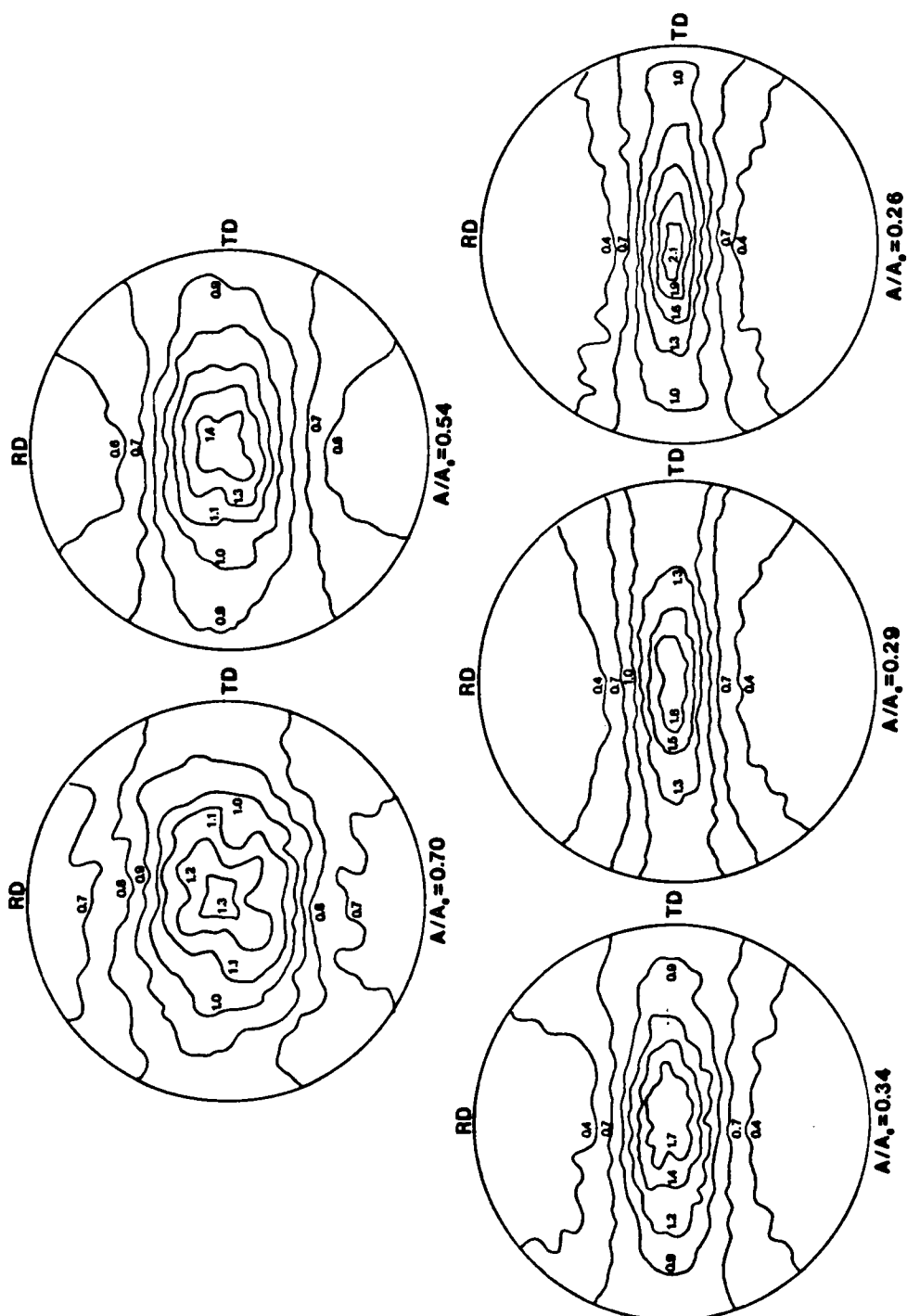


Figure 4C-5. (100) pole figures of Path II samples.

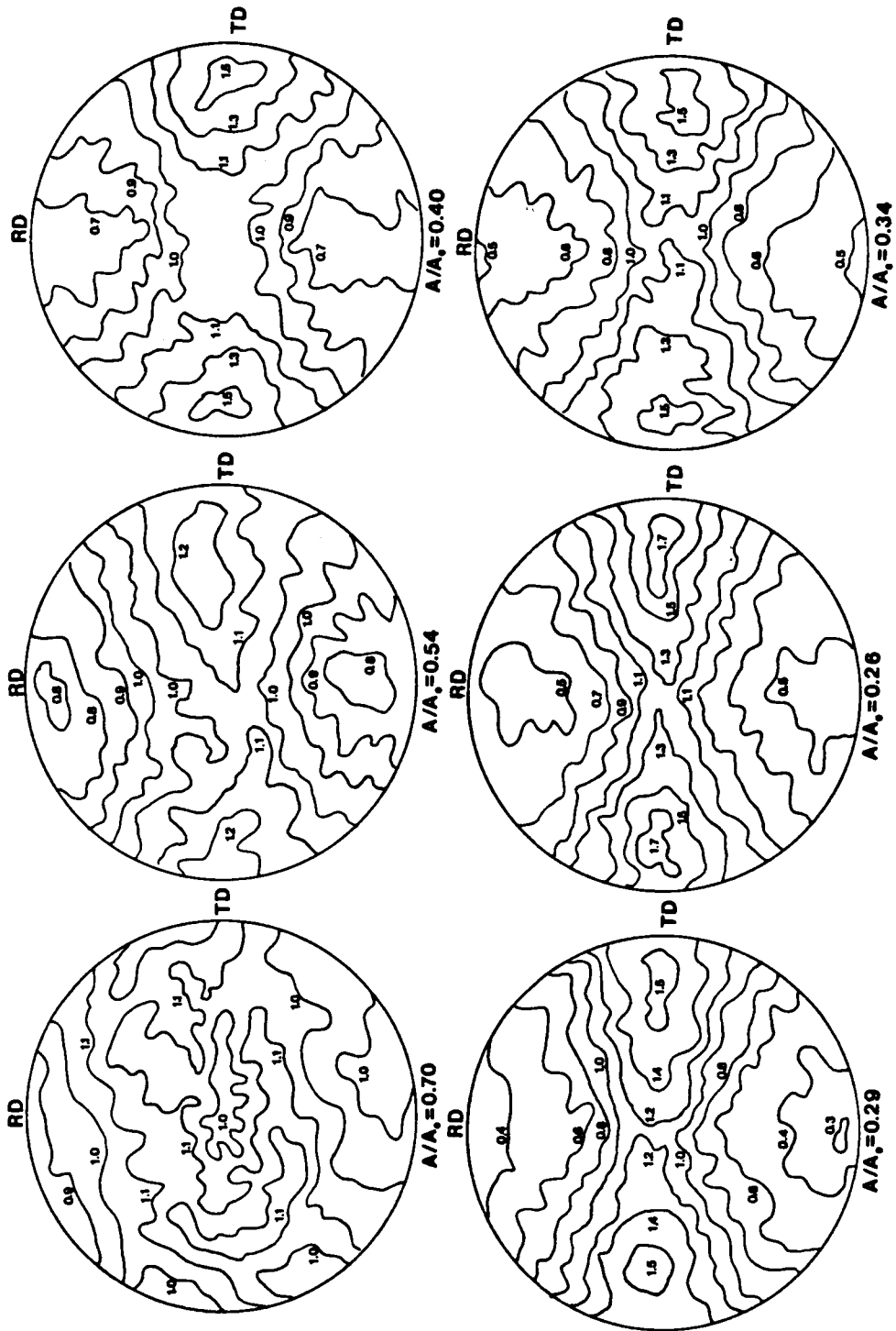


Figure 4C-6. (010) pole figures of Path II samples.

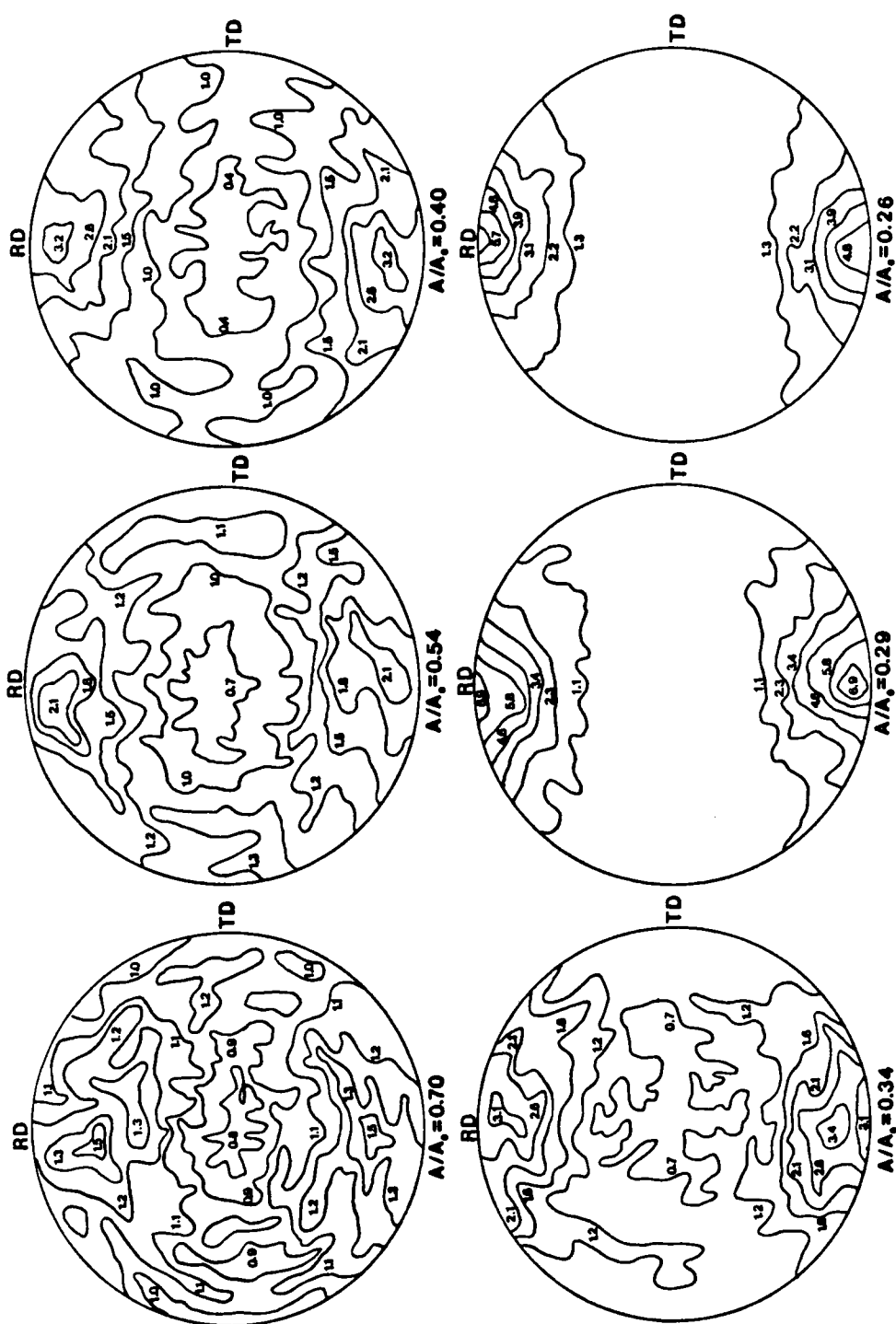


Figure 4C-7. (105) pole figures of Path II samples.

The (100) pole figures are shown in Figure 4C-8. At low roll reductions ($A/A_0 > 0.76$) little preferred orientation of the (100) plane is indicated.

At $A/A_0 = 0.57$, rolling has caused the (100) planes to rotate so that they show a preferential alignment in which the (100) normals are concentrated near the RD and at an angle to it. Two intensity maxima are observed at points about 30° to the RD in the RD-ND plane.

At $A/A_0 = 0.45$ these maxima have moved closer to the normal direction.

At $A/A_0 = 0.40$, most of the poles lie in a band centered about the equator. A strong maximum is noted in the normal direction. This indicates the (100) planes are aligning parallel to the RD with the preferred orientation being in the plane of the film. This tendency further increases at higher roll reductions ($A/A_0 < 0.40$), but a tendency for the (100) poles to spread toward the transverse direction is retained to the highest attainable rolling reductions. The alignment changes little below a reduction of 0.30.

These pole figures indicate the chains are becoming increasingly aligned perpendicular to the ND with increasing roll reductions. Furthermore, at high reductions the (100) planes become preferentially oriented in the plane of the film. The (010) pole figures are shown in Figure 4C-9. At low reductions ($A/A_0 = 0.57$), the (010) poles show weak maxima about the TD.

As rolling continues the intensity perpendicular to RD increases and the maxima move along the equator to points about 10° to 15° from

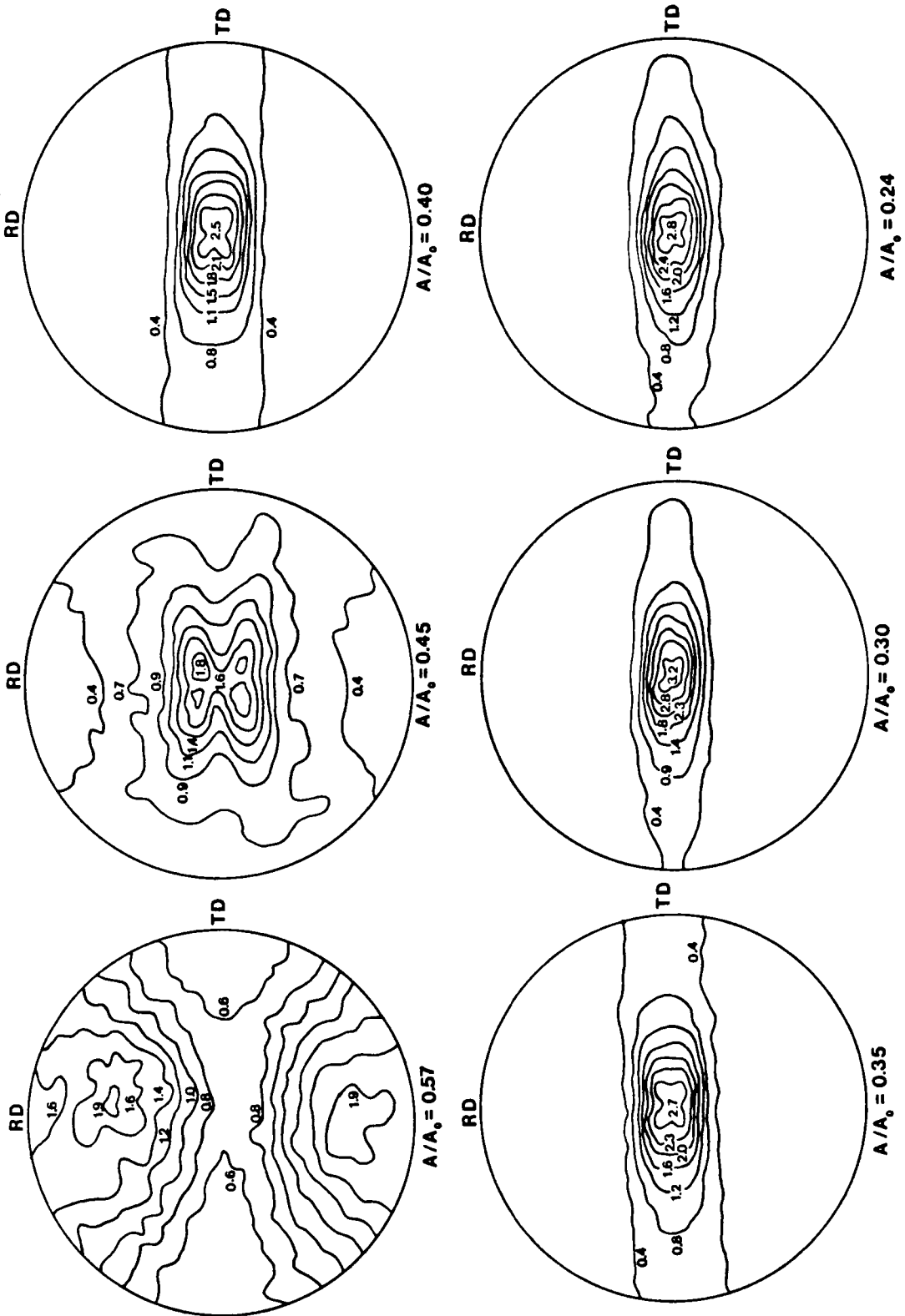


Figure 4C-8. (100) pole figures of Path III samples.

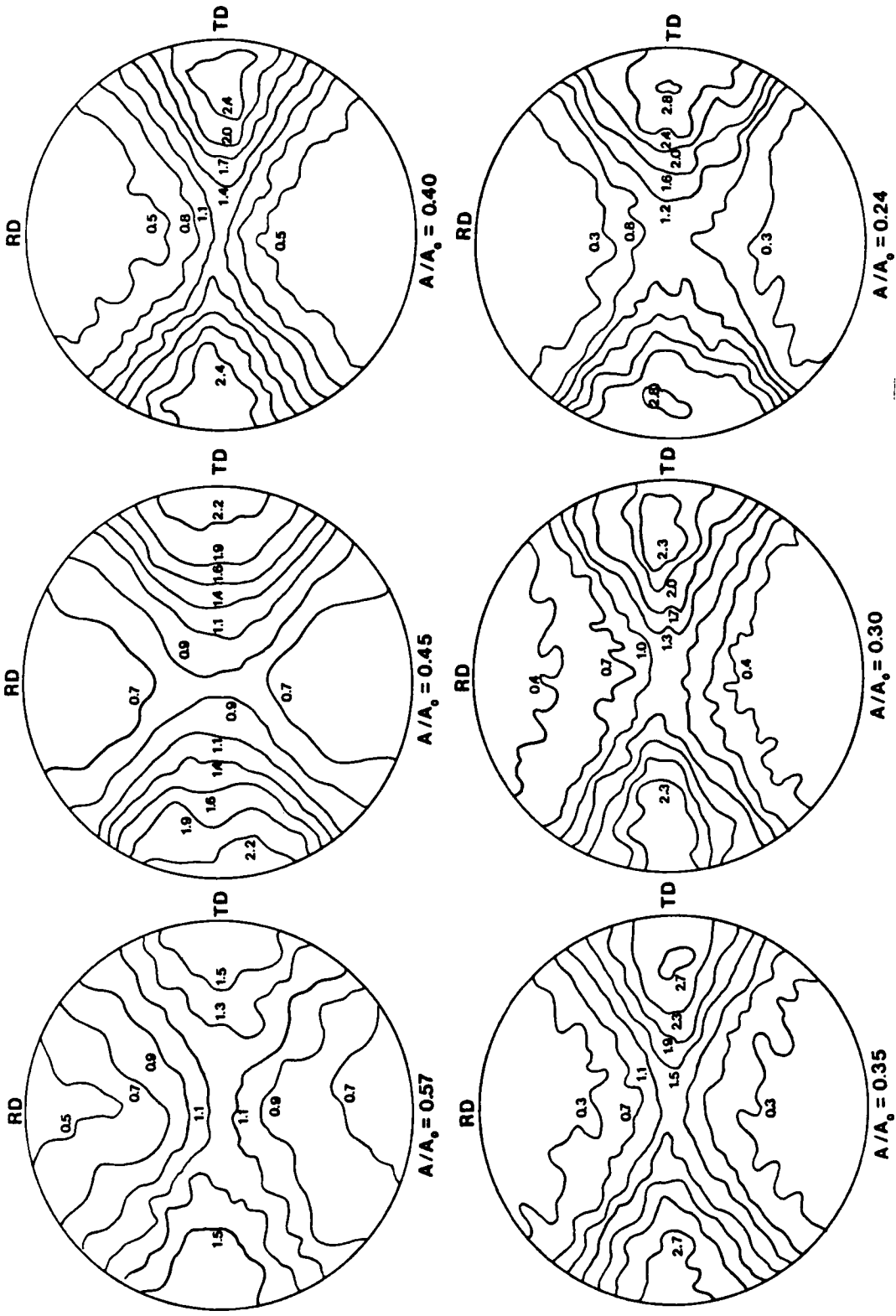


Figure 4C-9. (010) pole figures of Path III samples.

the TD. At the highest reduction these maxima have become sharper but have not moved in position.

These pole figures together with the (100) pole figures indicate the polymer chains are becoming preferentially oriented in the RD during rolling.

The $\bar{1}05$ pole figures for Path III are shown in Figure 4C-10. At low reductions, no preferred orientation is detected. At $A/A_0 = 0.45$, however, the pole figure suddenly shows a high concentration of poles in the roll direction. As reduction increases, the concentration of poles in the roll direction increases. This is further proof of the alignment of the chain axes in the roll direction. The strong intensity in the RD at high reductions indicates a high degree of orientation. This will be quantitatively described by orientation functions in a separate section.

Orientation Factors

For Path I, $\overline{\cos^2 \chi}$ values were obtained from the pole figure data taken at $2\theta = 21.5^\circ$. In this case χ is the angle between the normal to the (100) plane of the pseudohexagonal structure and the roll direction. From this value, an orientation factor " f_a " can be calculated. For a hexagonal system

$$f_c = -2 \cdot f_a \quad (4C.1)$$

where f_c is the chain axis orientation factor. Thus within the pseudohexagonal approximation for the paracrystalline structure, the chain axis orientation factor can be obtained from the pole figures shown in Figure 4C-4 (page 110).

In Paths II and III, the orientation factors were computed from the $(\bar{1}05)$ pole figures. These poles are a good measure of the chain axis orientation and can be used to compute Hermans' orientation factor, f_c , directly.

Figure 4C-11 shows f_c as a function of roll reduction for Paths I, II, and III. All three paths show increasing chain alignment in the roll direction with increasing roll reductions. Path I samples appear to orient more quickly and to a higher degree than Path II samples. Relatively little orientation occurs in Path II until high reductions ($A/A_0 < 0.4$) are achieved. It appears that the chains in initially crystalline material can not orient very easily until the lamellar structure is broken down. SAXS patterns give evidence of this breakdown as will be shown in a subsequent section. Path III samples also appear to be less oriented than Path I samples at a given reduction. Perhaps some of the orientation imparted during rolling is lost when the samples are heated above T_g . However, one can also argue that f_c is over-estimated for Path I as will be discussed later in this section.

Since orientation factors for Paths II and III were obtained in the same manner, one can safely assume a greater degree of chain alignment is achieved in Path III than in Path II.

Biaxial orientation functions for the chain axes were calculated for Paths I and III. $\overline{\cos^2 \chi}$ values were obtained from pole figures in the same manner as for the uniaxial case. In Path I, f_{az} and f_{ay} represent the orientation of a vector perpendicular to the chain axis with respect to the RD and the TD, respectively. Then, as explained before, we can calculate the orientation of the c-axis with respect to

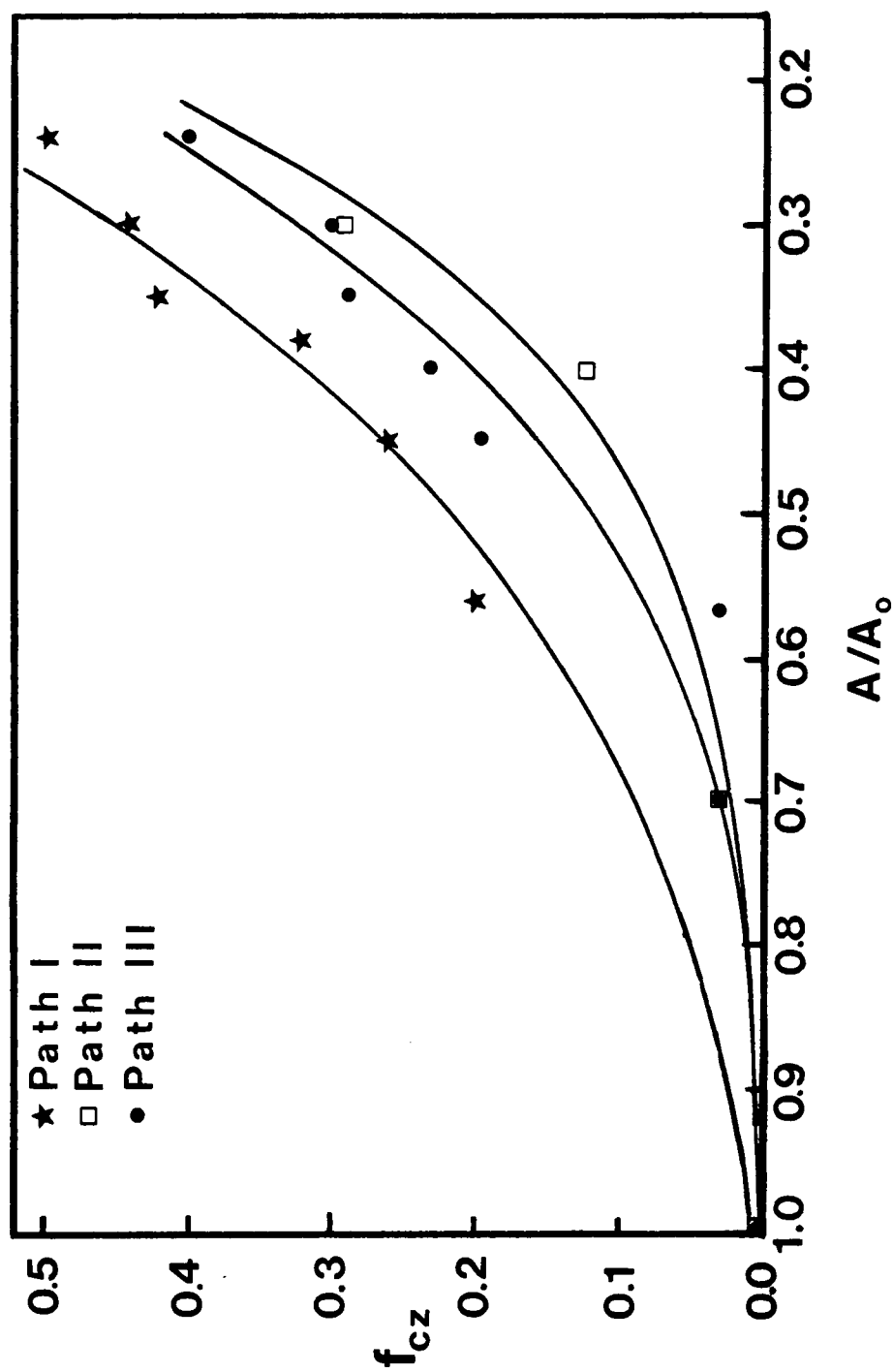


Figure 4C-11. Hermans' orientation factors as a function of roll reduction for Paths I, II, and III. For Paths II and III the factors were calculated from (105) pole figure data. For Path I the factor was calculated from pole figure data taken at $2\theta = 21.5^\circ$.

these reference axes

$$\begin{aligned} f_{cz} &= -2 \cdot f_{az} \\ f_{cy} &= -2 \cdot f_{ay} \end{aligned} \quad (4C.2)$$

In Path III f_{cz} and f_{cy} can be calculated directly from the $(\overline{105})$ pole figure data.

The biaxial orientation functions at different reductions for these two paths are shown in Figure 4C-12. For reference purposes, data for two cross-rolled PET samples are also shown. The reduction for the less oriented cross-rolled sample was $t/t_0 = 0.35$, while the reduction for the more oriented sample was $t/t_0 = 0.21$.

The data for Path I and III samples are shown scattered about the uniaxial line. This indicates there is little tendency for the chains to orient in the TD during conventional rolling as compared to cross-rolling.

The Path I samples, again, have a higher value of f_{cz} at a given roll reduction than the Path III samples, but it is questionable whether or not the chain alignment is actually greater.

The cross-rolled samples lie near the biaxial line showing that the chain axes are oriented almost equally in the roll and transverse directions. The chain axes in the sample rolled to $t/t_0 = 0.21$ show a much greater tendency to lie in the plane of the film than those of the less highly cross-rolled sample.

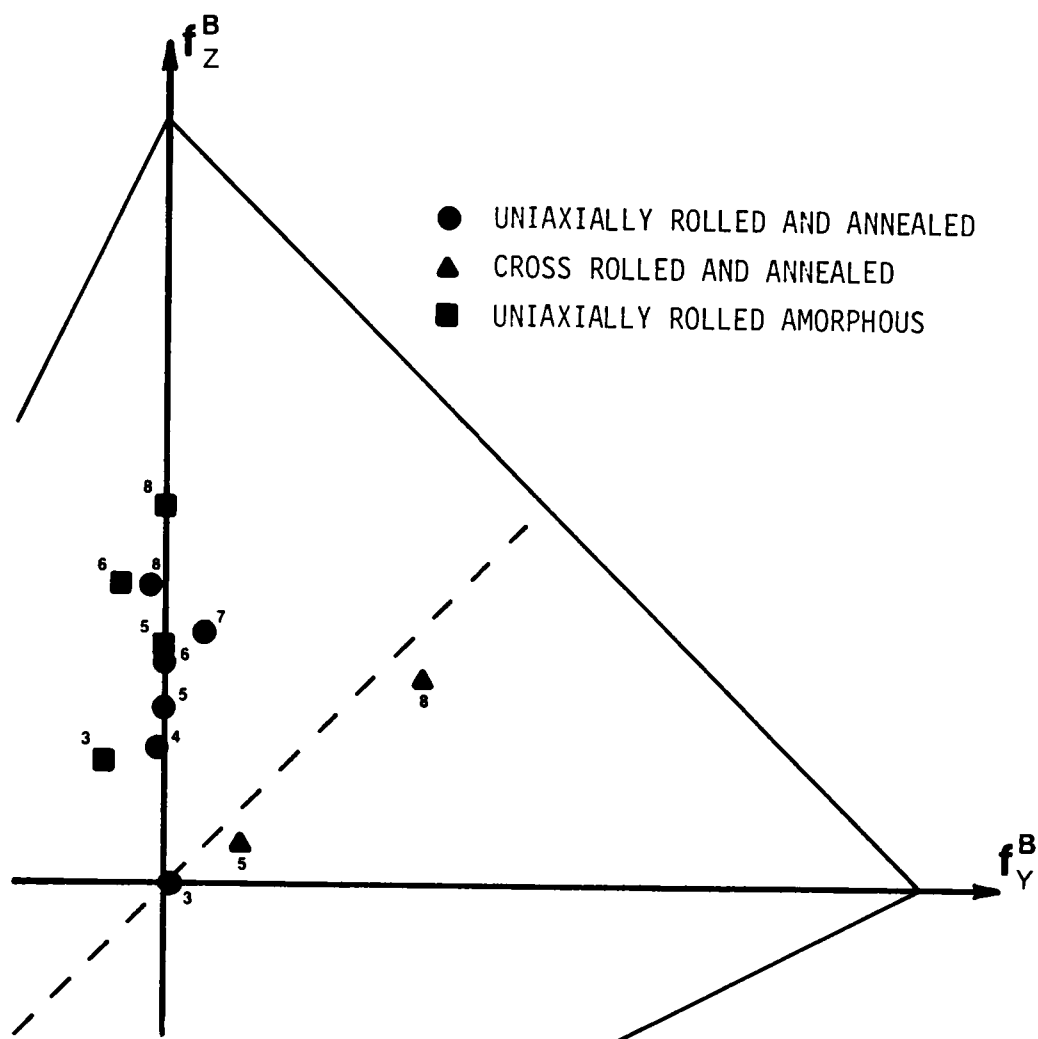


Figure 4C-12. Biaxial orientation functions for rolled PET. The sample numbers for Path I and III correspond to the roll reductions in Table 4A-1 (page 86) with 8 being the most highly rolled sample.

Discussion of WAXD Results

1. Flat Plate and Pole Figures

Path I (Amorphous). As previously noted, the diffraction from the Path I samples is probably due to the development of paracrystallinity and/or very small crystallites. Both morphologies would produce the significant broadening observed in these patterns. The more intense diffraction is probably due to some interchain distance related to the (100), (1 $\bar{1}$ 0), and (010) planes observed in crystalline material. If one assumes that this distance is the magnitude of a vector which is approximately perpendicular to the chain axis, then the patterns give information about the orientation of this vector and, hence, of the chains themselves. If we further assume that the chains tend to pack together in a pseudo-hexagonal arrangement, the peak at 21.5° (2θ) from which the pole figures in Figure 4C-4 (page 110) were made would represent the (100) reflection from the hexagonal structure. The pole figures would then represent the poles of these planes. On this basis both the pole figures and the flat plate patterns indicate that the chains are aligning with the rolling direction with increasing reductions in thickness.

At high reductions the intensity maximum about the ND in the pole figures indicates that the chains are preferentially oriented about their axes in some manner. Probably the benzene rings are preferentially oriented in the plane of the film as is the case for Path II and III samples.

Stress induced crystallization occurs during rolling and at the

higher reductions some discrete scattering is observed in the wide angle patterns indicating that the triclinic structure is developing. The sharp arc along the meridian at $2\theta = 25.9^\circ$ would correspond to a d-spacing of $3.44 \text{ \AA}$. This would appear to be a broadened reflection from the $(\bar{1}03)$ plane which has a d-spacing of $3.37 \text{ \AA}$. The broad, diffuse arc along the meridian with a peak 2θ of about 41° may be due to the $(\bar{1}05)$ plane which would be expected to diffract at 43° . The broad, intense spots along the equator indicate that the structure is still fairly paracrystalline. The ring that remains at a 2θ value of 14° is attributed to scattering by unoriented amorphous materials following Dumbleton and Bowles (19).

Path II (Crystalline). The WAXD pattern from the unrolled sample showed several distinct Debye rings. The most distinct rings were from the (010) , $(1\bar{1}0)$, and (100) crystalline planes all of which are parallel to the chain axis. As the samples are rolled the Debye rings concentrate in arcs about the equator in the patterns taken with the x-ray beam parallel to ND or TD. This indicates the chains are becoming preferentially aligned parallel to the RD.

Appreciable line broadening occurs at the higher roll reductions. This can be due to a very small crystallite size or to imperfections in the crystals due to strain or paracrystallinity. Probably during rolling the crystallites are crushed into very small fragments. Some distortion of the lattice structure and introduction of paracrystallinity is likely. This should be more prevalent at the highest roll reductions.

The patterns taken through the RD of the highly rolled films show

some "arcing" rather than continuous Debye rings. This is in contrast to patterns of fibers taken with the beam parallel to the fiber axis. Hence the orientation is not of the simple uniaxial type as in fibers, but of a more complex nature. Pole figures were used to analyze the structure further.

The pole figures show the (100) and (010) planes become preferentially oriented parallel to the roll direction during rolling. At the higher reductions the (100) poles show a maximum in the TD and the (010) poles show maxima along the equator about 15° from TD (85° from ND). The ($\bar{1}05$) pole figures show strong maxima in the roll direction at high reductions.

In order to interpret these results a review of the unit cell is in order (refer to Figure 3D-3 (page 75)). The angle between the (010) and (100) poles is 59.4° , the angle between the (010) and ($\bar{1}05$) poles is 80.2° , and the angle between the (100) and ($\bar{1}05$) poles is 85.2° . The angle between the chain axis and the ($\bar{1}05$) pole is 9.8° .

Two theoretical pole figures were drawn with these angles in mind.

In the first, the distribution of the (100), (010), and ($\bar{1}05$) poles are shown for an ideal sample in which all the chains are aligned in the roll direction but in which there is random rotation of the unit cells about the chain axes (see Figure 4C-13). The ($\bar{1}05$) poles lie in a circle about 10° from the RD. The (100) and (010) poles lie on the equator. There is uniform intensity about RD for the poles of all three planes.

If the (100) planes of the uniaxial case above were all aligned

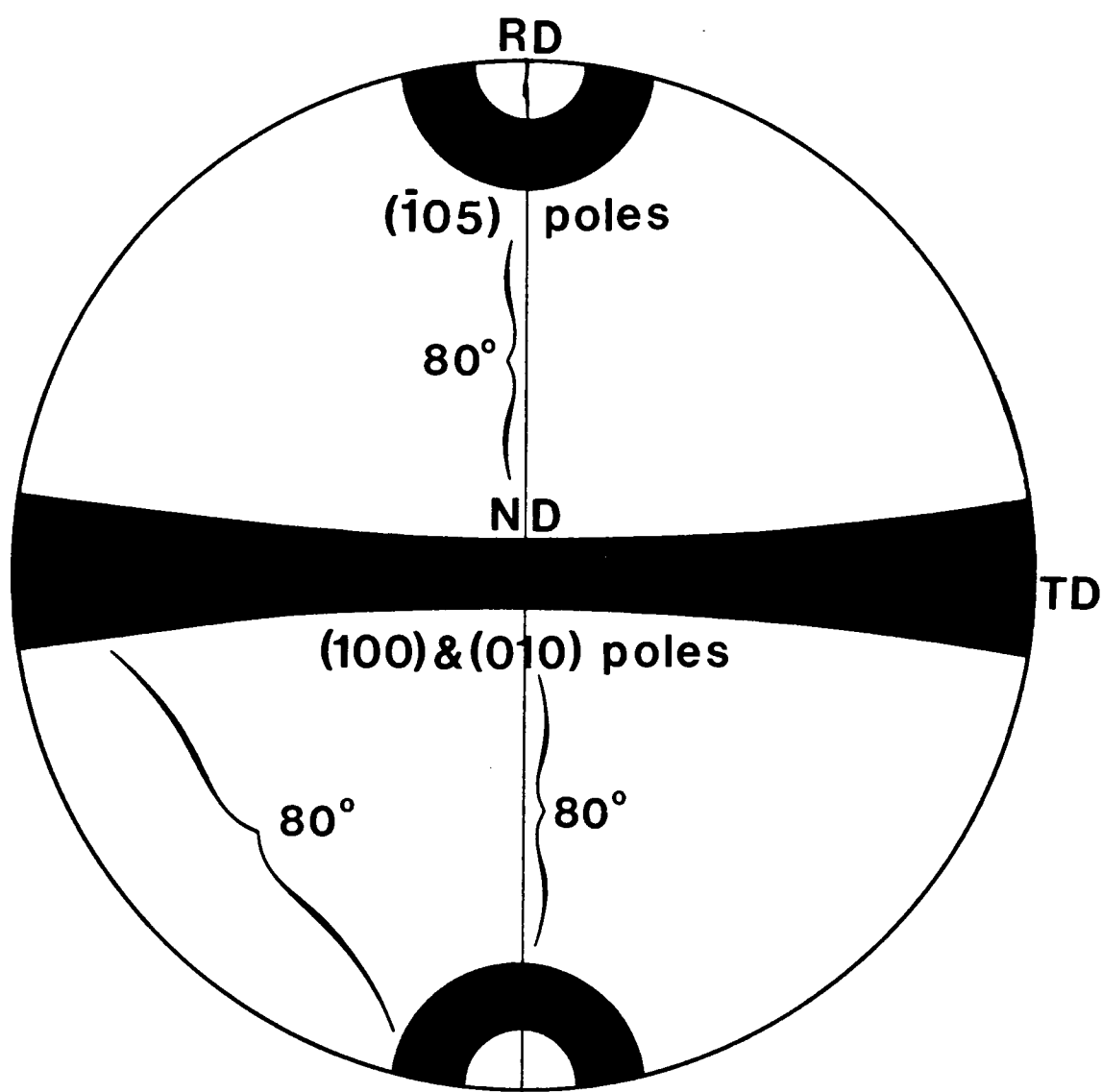


Figure 4C-13. Theoretical pole figure for PET film having perfect uniaxial orientation.

in the plane of the film, the pole figure in Figure 4C-14 would be obtained. The (100) poles would all be expected to lie in the ND. The (010) poles must lie 59.4° from the (100) poles along the equator because of the unit cell geometry and the condition that the chain axes be parallel to RD.

At the highest roll reduction, the experimental pole figures resemble something in between the two theoretical pole figures. The (100) poles show a maximum intensity in the ND and the (010) poles show maxima at 15° from TD. However, there is an appreciable amount of intensity all along the equator with considerable spread toward the RD in both these pole figures. The maximum in the (010) pole figure would be expected to appear at 30° to the TD if the orientation were exactly uniplanar axial.

The $(\bar{1}05)$ pole figure of the most highly rolled sample resembles that of the uniaxial case, except for the wide distribution of intensities about the RD.

The most reasonable picture of the morphology then is one in which most of the chains are distributed within some angular range about RD. This range decreases with rolling and is from 0° to 30° for the most highly rolled sample ($A/A_0 = 0.26$).

At the higher reductions the benzene rings begin to align parallel to the plane of the film. This explains the maximum in the ND of the (100) pole figures.

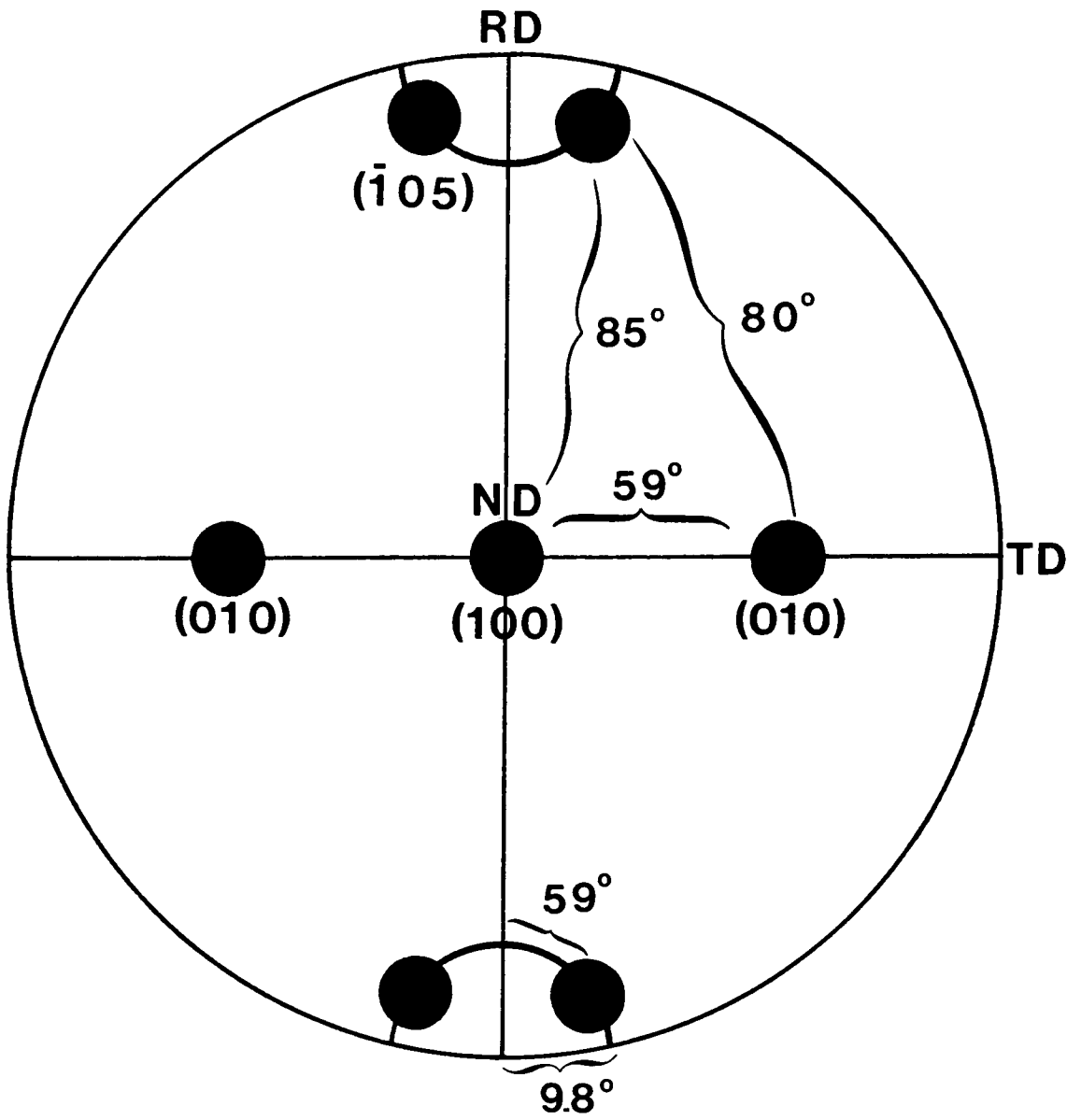


Figure 4C-14. Theoretical pole figure for PET film having perfect "uniaxial planar" orientation.

Path III (Rolled and Annealed). WAXD patterns of unrolled and moderately rolled samples show several distinct Debye rings. As the roll reduction increases, the Debye rings become well-defined arcs. The (100), (010), and ($\bar{1}\bar{1}0$) diffraction spots lie on the equator in the ND and TD patterns. Since these planes are parallel to the chain axis this suggests the chains are becoming aligned parallel to the RD. At the highest reduction, the ND patterns resemble those of a highly oriented fiber. The pattern taken with the beam parallel to RD, however, is quite different from that expected for a fiber. The (100) reflection is concentrated about the equator, and the (010) about the meridian, while the ($\bar{1}\bar{1}0$) reflection shows four maxima. Hence, the morphology is not of the simple uniaxial (fiber) type.

To investigate this complex morphology more thoroughly, WAXD pole figures were made of the (100), (010), and ($\bar{1}05$) planes at each level of reduction.

The pole figures show that at the highest reduction most of the normals to the (100) planes lie within a band 10° to 20° from the equator with the maximum intensity in the ND.

At high reductions, the (010) pole figures show two maxima on the equator about 10° to 15° from TD.

The ($\bar{1}05$) pole figures show intense maxima in the RD at the higher reductions.

To interpret these pole figures they were compared to the theoretical pole figures discussed in the previous section.

At moderate roll reductions the pole figures show some of the features of the theoretical pole figure for a uniaxially oriented sample.

The (100) and (010) poles are distributed in a wide band about the equator without the strong maxima seen in the uniplanar-axial case.

At high roll reductions the pole figures tend to resemble the theoretical uniplanar-axial case. The (100) poles show a strong maxima in the ND, although there is some spread of intensity along the equator. The (010) poles show weak maxima along the equator about 10° to 15° from the TD. This is in fair agreement with the model which predicts maxima along the equator 30° from the TD. The $(\bar{1}05)$ pole figure has strong intensity maxima in the RD. This is in good agreement with the model which predicts four maxima at 9.8° to the RD.

The discrepancies between the experimental and theoretical pole figures are probably due to the angular distribution of chains about the RD and the imperfect alignment of the (100) crystallographic plane in the plane of the film.

2. Orientation Factors

Hermans' orientation factors for the three paths indicated increasing alignment of the chains with the roll direction with increasing rolling reductions. At any given reduction f_c for the three paths showed the following order

$$\text{Path I} > \text{Path III} > \text{Path II}$$

The orientation factor f_c for Path I, however, may be somewhat overestimated due to the imperfection of our pseudo-hexagonal model. The model assumes that the diffraction at $2\theta = 21.5^{\circ}$ does not depend upon the orientation of the chains about their axes; i.e., the chains are modeled as long cylinders. The chains, however, are not true cylinders and

diffraction is dependent upon the orientation of the chain about its axis. Hence, f_c is not exactly equal to $-2f_a$. For example, take the extreme case of crystalline (100) planes aligned parallel to the plane of the film, but with the chain axes distributed randomly in RD-TD plane. The normals to the (100) planes would all point in the normal direction and f_a would be -0.5. According to equation 4C.1 f_c would be 1.0 when in actuality f_c is closer to 0.

Hence, one must be careful in making direct comparisons of f_c for Path I with either Path II or III.

D. SAXS

Introduction

A series of SAXS patterns were made as a function of roll reduction for the various samples of Paths I, II, and III. Patterns were obtained with the samples oriented in each of three mutually perpendicular directions: with the x-ray beam coincident with the roll, transverse, and normal directions.

The dimensions of the various patterns were then measured and recorded. The following conventions are used in naming these dimensions. The diameter of the ring shaped patterns and the distance between the lobes of the two-point patterns are defined as "A" and are used to calculate the long period. In the four-point patterns, the diagonal distance between the lobes is "B," the vertical distance is "C," and the horizontal distance is "D." The angle between two lobes on either side of the ND or TD direction is defined as " β ." These relationships are shown in Figure 4D-1.

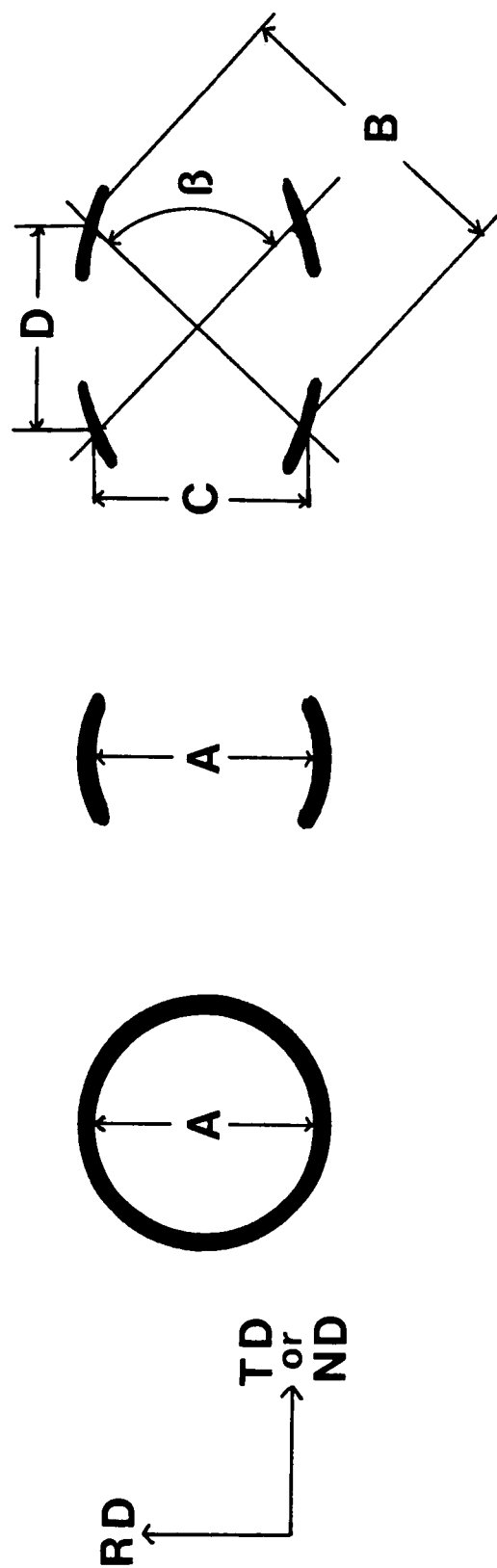


Figure 4D-1. Schematic diagram showing the various periodicities measured from the SAXS patterns.

Results

1. Path I (Amorphous)

No obvious small angle x-ray scattering patterns were observed for the rolled amorphous samples. Any scattering occurring in the small angle range was too diffuse and too weak to be detected and measured with the film recording technique used in this investigation.

2. Path II (Crystalline)

The SAXS patterns obtained for these samples are shown in Figure 4D-2. In general, these patterns became less intense with increasing reduction by rolling.

A ring shaped pattern was observed for unrolled samples. This ring shaped pattern probably arises from the overall random orientation of the scattering entities in the sample.

With the x-ray beam parallel to the ND a ring shaped pattern is obtained down to a roll reduction of $A/A_0 = 0.54$. At $A/A_0 = 0.40$, the pattern is circular but a very faint cross shape is visible. At higher reductions the intensity on the equator becomes negligible and the elliptical shape becomes a broad two point pattern.

With the beam in the TD, a distinct cross shape is observed on a circular background at $A/A_0 = 0.86$. Four maxima are present. At $A/A_0 = 0.54$, a strong four-point pattern is observed. With higher reduction the four point pattern becomes less distinct and more elliptical in shape. At still higher reductions ($A/A_0 < 0.34$) the intensity decreases greatly and the four-point pattern appears smeared in the equatorial direction.

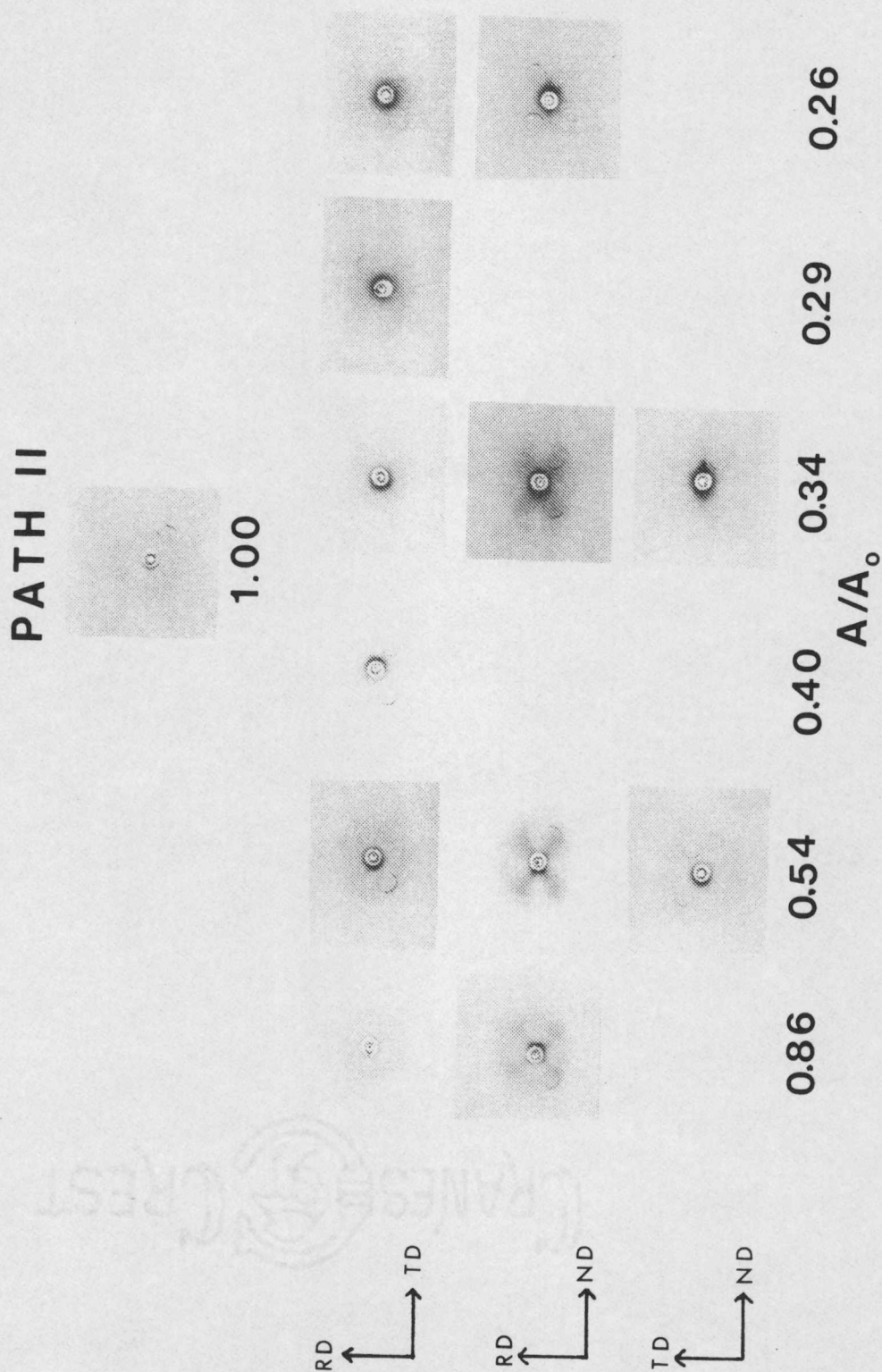


Figure 4D-2. SAXS patterns obtained for Path II samples.

With the beam in the RD, the ring shaped pattern observed in the unrolled samples becomes much weaker with rolling and changes at moderate reductions to an elliptical shape and at high reductions to a fainter more elongated ellipse. Table 4D-1 shows the various spacings calculated from the patterns. The apparent periodicities calculated from patterns taken with the x-ray beam parallel to ND remain almost constant up to roll reductions of 0.54. At higher reductions, no distinct periodicity could be detected.

The periodicity computed from distance "B" (Figure 4D-1) in patterns with the x-ray beam parallel to TD decreased with increasing reductions down to $A/A_0 = 0.34$. At higher reductions no periodicity could be detected.

The angle β decreased with increasing roll reductions.

3. Path III (Rolled and Annealed)

SAXS patterns as a function of roll reduction are shown in Figure 4D-3 for the rolled and subsequently fixed annealed samples. With the beam parallel to ND or TD, a distinct scattering pattern is observed at all reductions, unlike Path II.

For patterns taken with the beam parallel to ND a ring shape is observed for unrolled samples. The ring shape gradually changes into a two-point pattern as the roll reduction increased. At very high reductions, the lobes in two-point patterns become elongated parallel to the equatorial direction. At the highest reduction ($A/A_0 = 0.24$), a slight tendency toward formation of a four-point pattern is observed.

With the beam parallel to the transverse direction the initial

TABLE 4D-1
SPACINGS FROM SAXS PATTERNS OF PATH II SAMPLES¹

A/A ₀	Thru ND	Thru TD				
	A	A	B	C	D	β
1.00	99	99				
0.86	99		95	137	137	90 ⁰
0.70	99					
0.54	95		88	155	112	72 ⁰
0.40	- ²					
0.34	- ²					
0.29	- ²					
0.26	- ²					

¹ All dimensions are in Angstroms.

² Patterns from samples rolled to A/A₀ < 0.54 were too diffuse to determine spacings.

PATH III

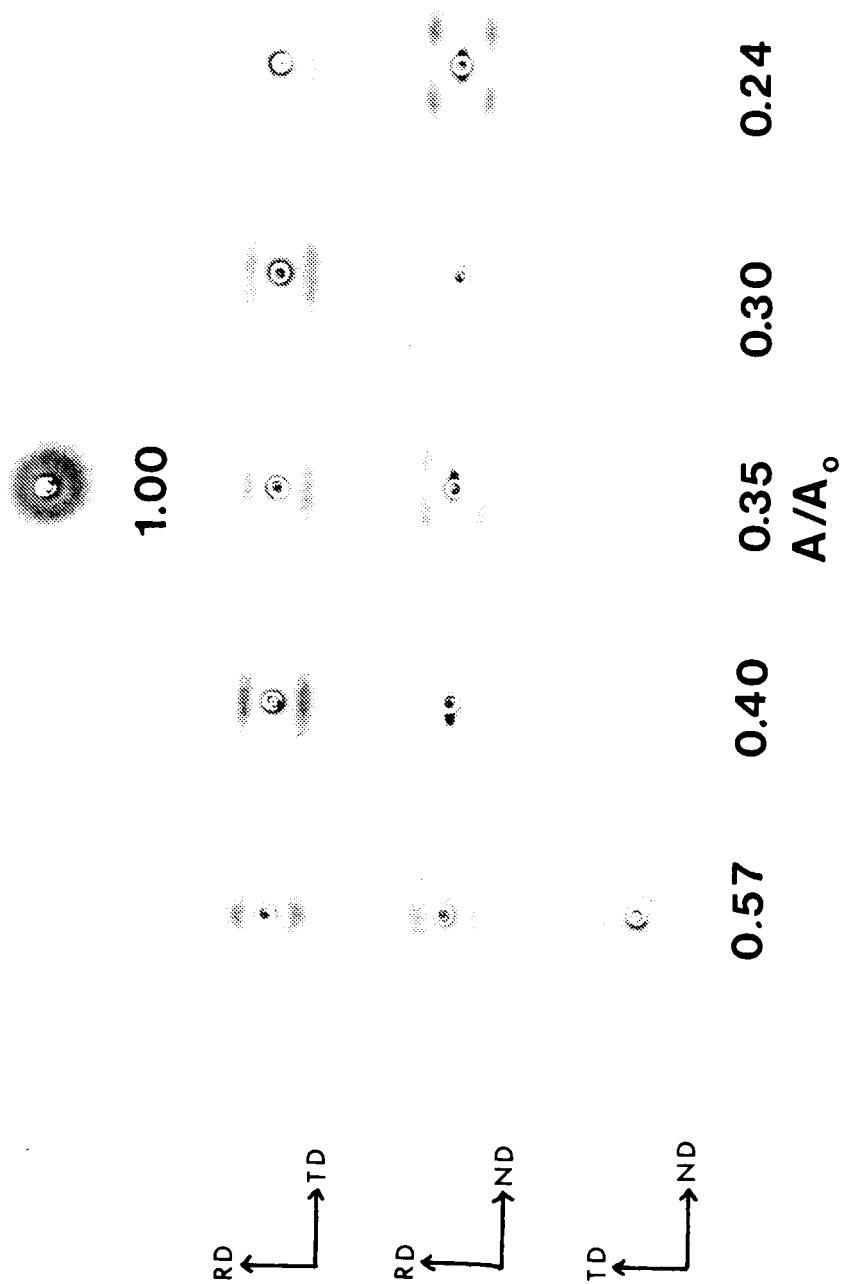


Figure 4D-3. SAXS patterns obtained for Path III samples.

ring shaped pattern changes with rolling and becomes less intense along the equator. With further reduction by rolling it changes into a two-point pattern which is elongated parallel to the equator. At reductions greater than $A/A_0 = 0.40$ a four-point pattern develops as shown in Figure 4D-3.

With the beam in the roll direction the ring shaped pattern observed in the unrolled sample grows larger in diameter and becomes weaker in intensity as higher reductions are achieved.

Table 4D-2 summarizes the various periodicities calculated from the Path III samples. With the x-ray beam parallel to ND or TD, the periodicity calculated from dimension "B", Figure 4D-1, decreases slightly at first and then remains constant at about $103 \text{ \AA}$ upon further rolling. No distinct periodicity is observed at moderate and high roll reductions with the samples oriented so that the beam is parallel to the RD.

In the four-point patterns the periodicity corresponding to the distance "C" does not change much with rolling, whereas the spacing corresponding to "D" decreases with rolling.

The angle β decreases with rolling.

Discussion of SAXS Patterns

1. Path I (Amorphous)

As previously noted SAXS patterns could not be detected for these samples. Apparently the crystallinity is too low to provide appreciable SAXS, especially in the absence of regular chain folding.

TABLE 4D-2
SPACINGS FROM SAXS PATTERNS OF PATH III SAMPLES

Through ND					
A/A_0	A	B	C	D	β
1.00	108 $\overset{0}{\text{\AA}}$				
0.76	-				
0.57	103				
0.45	-				
0.40	103				
0.35	103				
0.30	103	88	103	137	106 ^{0}
0.24	103	82	112	124	95 ^{0}
Through TD					
A/A_0	A	B	C	D	β
1.00	112 $\overset{0}{\text{\AA}}$				
0.76	-				
0.57	103				
0.45	-				
0.40	103	88	112	137	101 ^{0}
0.35	103	77	112	112	90 ^{0}
0.30	-	73	112	95	80 ^{0}
0.24	-	69	112	88	76 ^{0}

2. Path II (Crystalline)

Spherulites are believed to form during annealing at 150°C (39, 90, 93). The discrete scattering observed in all the SAXS patterns is presumed to arise from lamellar or fibrillar structures formed in the spherulites during annealing. Rolling deforms these structures and high reductions produce so many defects that a degree of diffuseness is introduced into the patterns. This complicates the morphological interpretation of the patterns.

A schematic model of the morphology (Figure 4D-4) was devised to help explain the SAXS patterns.

The ring shaped patterns observed in the unrolled samples appear to result from the random orientation of the lamellar structures which make up the spherulites.

Upon rolling the spherulites are deformed into elliptical shapes with some of the lamellae tilted at some preferred angle to the RD. The cross shaped part of the patterns taken with the TD parallel to the beam is due to these oriented lamellae while the ring shaped part is due to the remaining unoriented lamellae. At $A/A_0 = 0.86$, a large percentage of the lamellae appear to remain unoriented. At $A/A_0 = 0.54$, the most intense four-point pattern is observed, indicating the maximum number of lamellae have been oriented by rolling. At higher reductions the patterns grow weaker and more diffuse. Apparently, the spherulites become further crushed and the lamellae begin to break into chunks.

At still higher reductions ($A/A_0 < 0.34$), the SAXS patterns are too weak and diffuse that it must be concluded that there is little periodicity remaining. At these reductions the WAXD patterns show

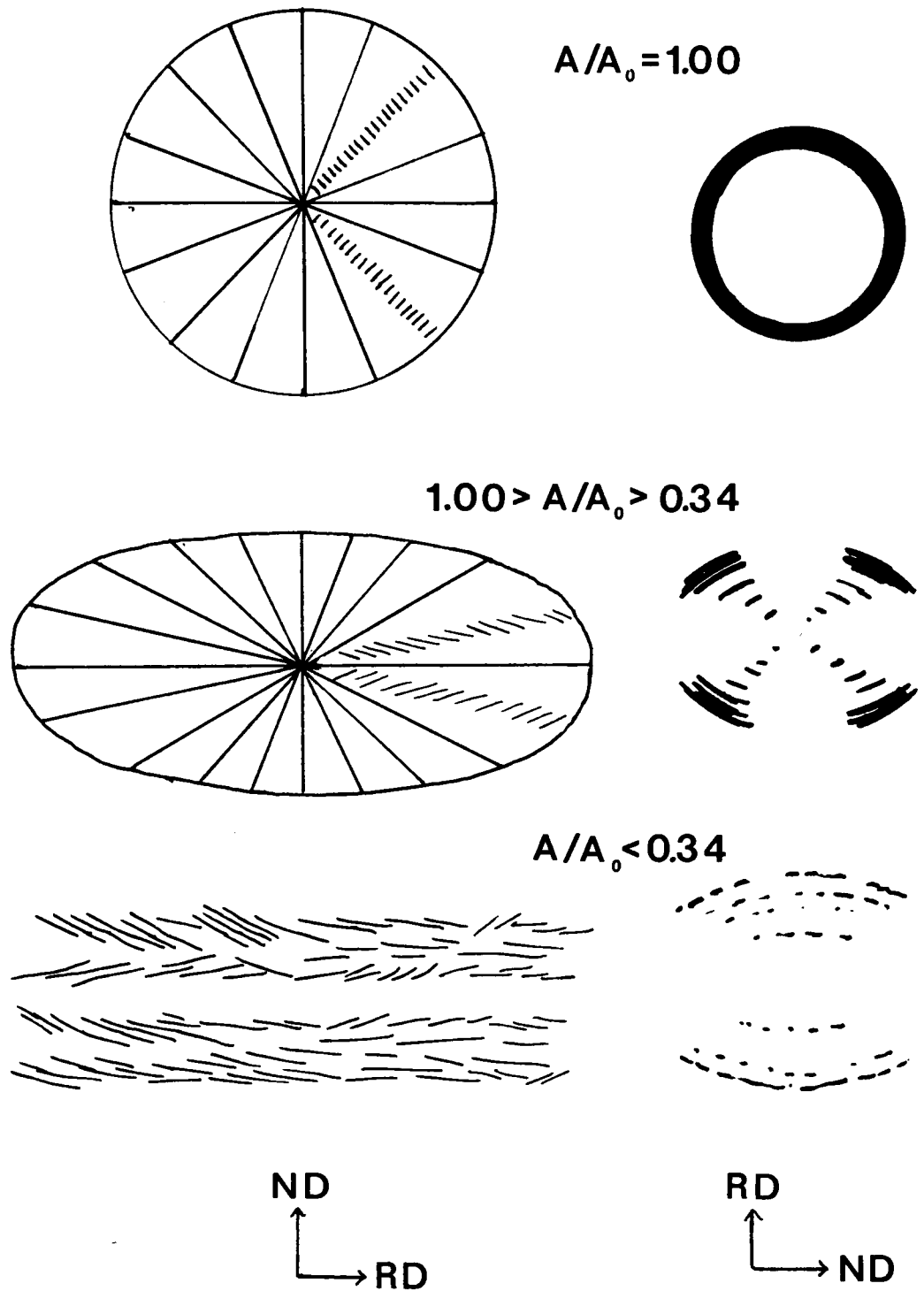


Figure 4D-4. Morphological models (left) used to explain the SAXS patterns (right) obtained for Path II samples.

extensive peak broadening. Pole figures also indicate a sudden increase in alignment of the chain axis with the roll direction at these reductions ($A/A_0 < 0.34$), as shown in Figure 4C-7 (page 114).

The angle β is presumed to be twice the average angle between a lamellar face and the RD. The decrease in β with increasing reduction indicates the lamellar faces are tilting toward the TD during rolling as shown in Figure 4D-4.

3. Path III (Rolled and Annealed)

The SAXS patterns show a ring shaped pattern before the samples are rolled. Upon moderate rolling the patterns taken with the x-ray beam parallel to the ND or TD, change into two-point patterns. At high roll reductions, four-point patterns are observed in the patterns taken with the x-ray beam parallel to the TD.

A model is proposed in Figure 4D-5 which is consistent with the observed changes during rolling.

Spherulites are believed to form in the unrolled samples upon annealing (39, 90, 93). Since the lamellae in spherulites are, on the average distributed randomly in space, the ring shaped SAXS pattern is explained.

Chain folding in oriented and annealed PET seems to be a reasonable assumption, based on the work of Koenig and Hannon (46) and Prevorsek and Sibilia (59). Hence, some regular chain folding is believed to occur in the rolled and annealed samples.

As the PET films become oriented during rolling, some line nuclei are formed from adjacent extended chains. Upon subsequent annealing

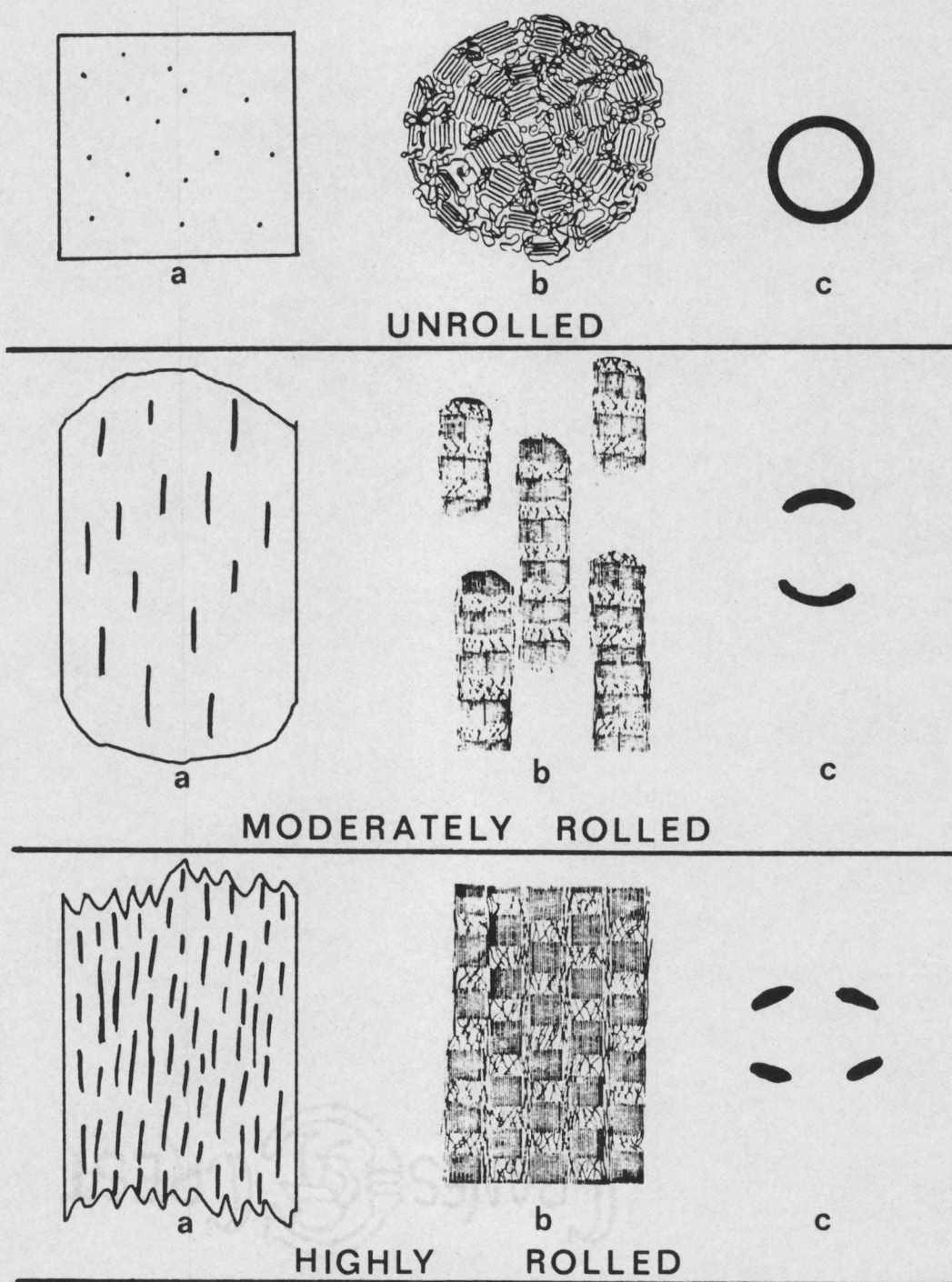


Figure 4D-5. Morphological model of rolled and annealed (Path III) samples. Nucleation sites (a) existing in the samples or produced by rolling give rise to spherulites or cylindrites (b) during annealing. Idealized SAXS patterns are shown in (c). The roll direction is vertical and the transverse direction is horizontal.

folded chain lamellae grow epitaxially from these line nuclei. This produces structures that may be called "cylindrites" and are similar to the row nucleated structures observed by Keller and Machin (40) in polyethylene crystallized from an oriented melt. In such a model the chain folded crystals would grow in the TD while the chains would lie parallel to the RD. The two-point patterns observed with the moderately rolled samples with $A/A_0 < 0.57$ must originate from the lamellae within these oriented cylindrites. At low reductions, $A/A_0 > 0.40$, the morphology appears to be intermediate between a spherulite and cylindrite structure.

The broadening of the two-point patterns in the direction parallel to the equator and subsequent development of the four-point patterns, especially in patterns taken with the beam parallel to the transverse direction, can be explained as follows. As roll reductions increase more nuclei are formed. Upon annealing, more cylindrites would form, but their growth would be limited by neighboring cylindrites. Hence, the lateral dimension of the cylindrite would decrease with rolling causing the broadening of the two point pattern. Each cylindrite would consist of alternate crystalline and amorphous regions. It is possible, that due to competition by growing crystallites for chains from amorphous regions, the cylindrites form in a staggered arrangement. That is, the amorphous regions of one cylindrite would be next to the crystalline region of an adjacent cylindrite. The four-point pattern arises from the staggered arrangement of crystallites as shown in Figure 4D-5.

The angle β between the peaks in the four-point pattern decreases

with increasing reduction. This can be explained by a decrease in the radial dimension of the cylindrites. As the cylindrites decrease in width the effective angle α between diagonal rows of crystallites is increased. This translates to a decrease in the angle β in reciprocal space as shown in Figure 4D-6.

The morphological model presented here exhibits some of the features of previous models developed for drawn fibers and films.

Prevorsek et al. (59, 60) presented the models shown in Figure 4D-7 to explain the two and four-point SAXS patterns observed for drawn and annealed PET and nylon fibers. The two-point pattern arises from microfibrils in which the crystalline regions lie adjacent to each other while the four-point pattern arises from a staggered arrangement of the crystallites.

Fischer and Fakirov (27), based on SAXS and electron microscopy results, report that regular chain folding occurs in highly drawn and annealed PET bristles, but that there is no evidence of a fibrillar structure. They further report, however, that the breadth of the peak in the two-point SAXS patterns indicate some type of periodicity perpendicular to the draw direction. This was corroborated by electron microscopy results which showed the samples fibrillated upon breaking. The authors conclude that "if a fiber structure is already present in the unbroken sample, density fluctuation must be very small."

Fischer and Fakirov explain the morphology in drawn and annealed PET bristles in terms of a "paracrystalline layer lattice" in which there are "various kinds of longitudinal (along the fiber axis) and lateral arrangements of crystalline blocks." They conclude that the

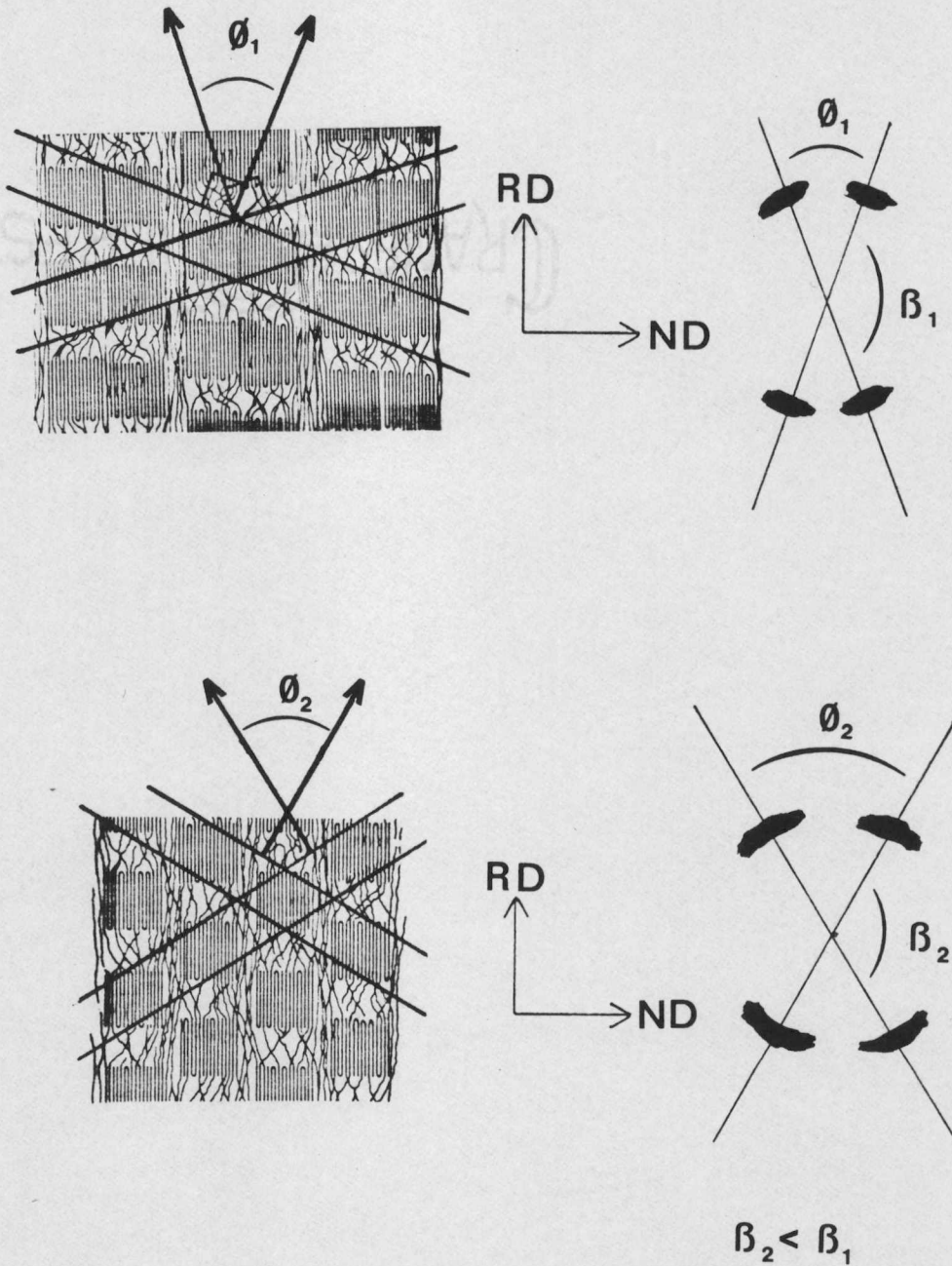


Figure 4D-6. The decrease in the angle β can be explained by the decrease in the width of the crystallites.

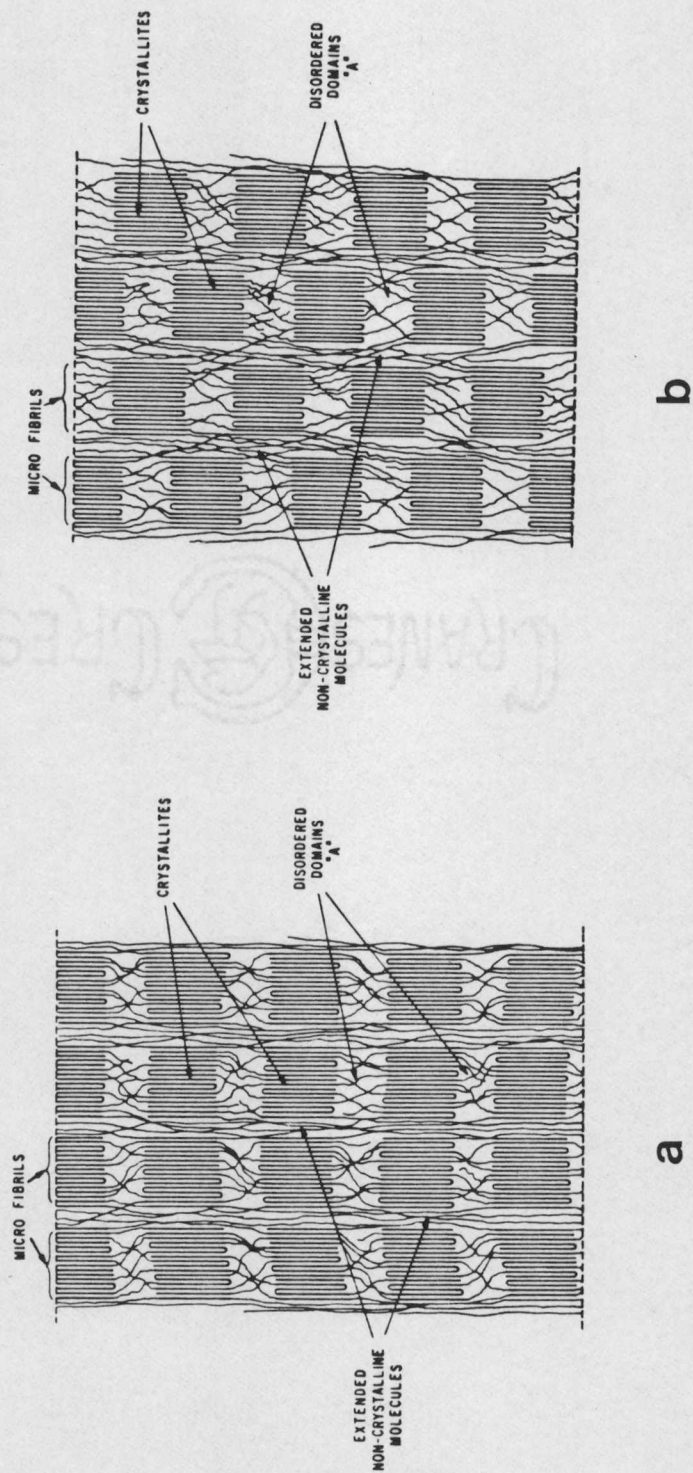


Figure 4D-7. Schematic structure of PET fibers giving rise to (a) two-point and (b) four-point patterns. Fiber axis is vertical.

Source: D. C. Prevorsek et al., J. Macromol. Sci. - Phys., B9, 733-759 (1974); D. C. Prevorsek et al., J. Macromol. Sci. - Phys., B8, 127-156 (1973).

lateral growth of the crystalline blocks is "only possible by additional chain folding and staggering, since growth is hindered by chains which are already incorporated in other mosaic [crystalline] blocks."

So, presumably, their four-point patterns arise from a mosaic or staggered arrangement of crystallites in agreement with the model presented in this thesis.

Our model also shows some resemblance to the one proposed by Statton and Godard for drawn PET films (74). Their model consists of sheets of lamellae which are stacked together in such a manner that the crystallites in one sheet are adjacent to the amorphous regions in the two sheets on either side. However, they explain their model in terms of extended chain crystallites or fringed micelles, while the model presented in this thesis incorporates folded chain crystallites.

E. MECHANICAL TESTING

General Features of the Stress-Strain Curves

The different processing paths and levels of reduction produced many differently shaped stress-strain curves. Figure 4E-1 is an attempt to show an overall qualitative view of the different types of curves encountered.

Actual values for the mechanical properties (modulus, yield strength, ultimate strength, and elongation to break) are given in Appendix B.

Figure 4E-2 is a comparison of quantitative stress-strain curves of unrolled PET for the three processing paths. Note the decreased elongation to break in the crystalline samples (Paths II and III).

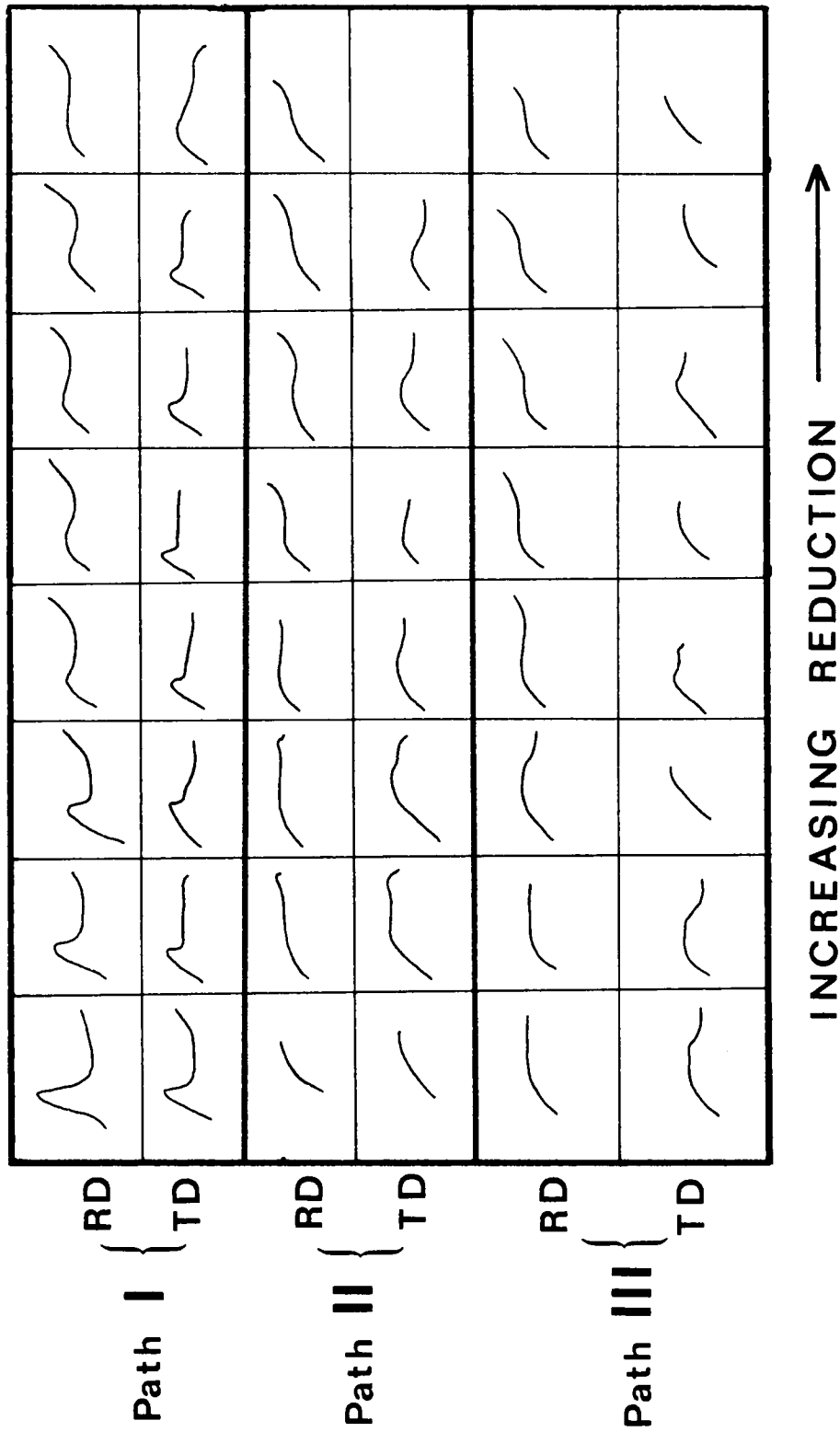


Figure 4E-1. Qualitative sketches of the various types of stress-strain curves encountered for Path I, II, and III samples.

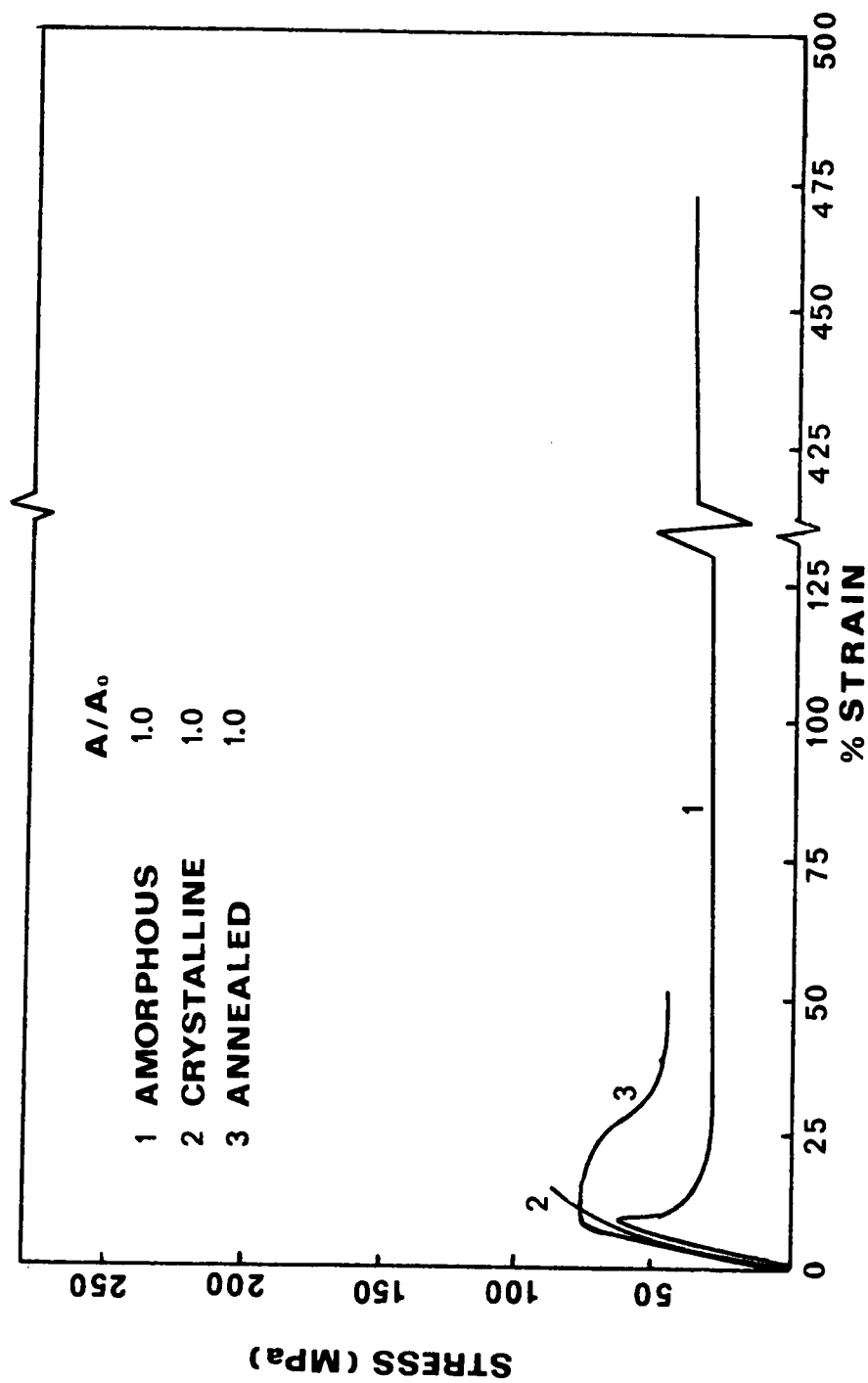


Figure 4E-2. Stress-strain curves for unrolled samples.

Figures 4E-3, 4E-4, and 4E-5 compare RD and TD samples at high reductions for Paths I, II, and III respectively.

The elongation to break is greater in the RD, except for highly rolled Path II samples. The modulus, stress at yield, and tensile strength are greater in the RD for these three paths.

Results

1. Modulus

The modulus is shown as a function of the roll reduction in both the roll and transverse directions in Figures 4E-6 and 4E-7, respectively, for Paths I, II, and III.

In general the modulus increased in the RD with rolling for all three paths. At the highest reductions ($A/A_0 < 0.35$) the modulus decreased in the order Path II $\geq$ Path III $>$ Path I. However, the difference between Path II and Path III values appears to be of the same order as the experimental error.

The modulus in the TD changed little with rolling, showing only a slight decrease at the higher reductions. The modulus was greatest at all reductions for Path III samples, followed by Path II samples.

2. Yield Strength

The yield strength as a function of the roll reduction is shown in Figures 4E-8 and 4E-9 for the roll and transverse directions, respectively, for Paths I, II, and III.

The yield strength in the RD showed only modest improvements with rolling. In general, the Path III samples had the highest yield strength by a slight margin.

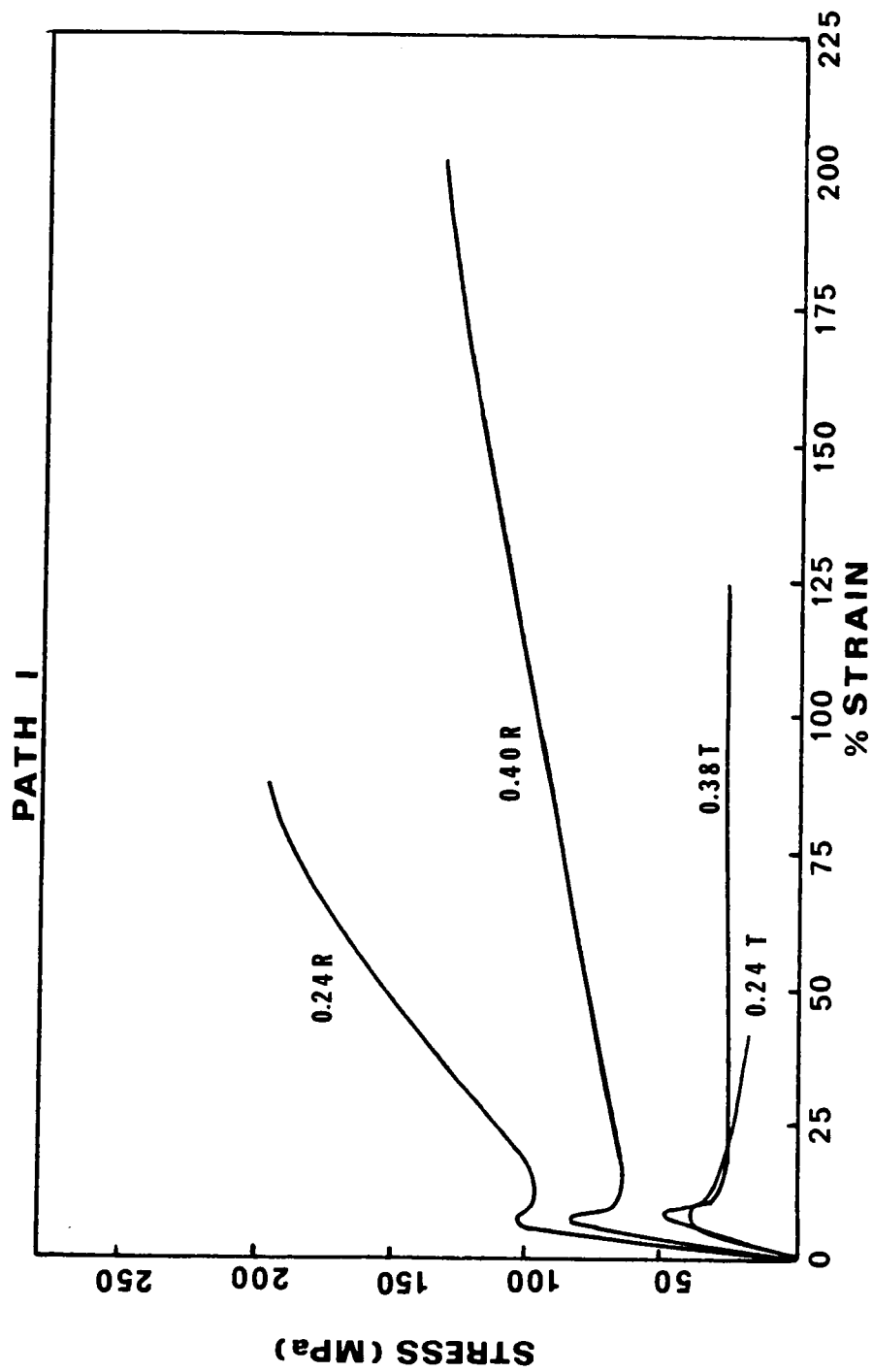


Figure 4E-3. Stress-strain curves for Path I samples.

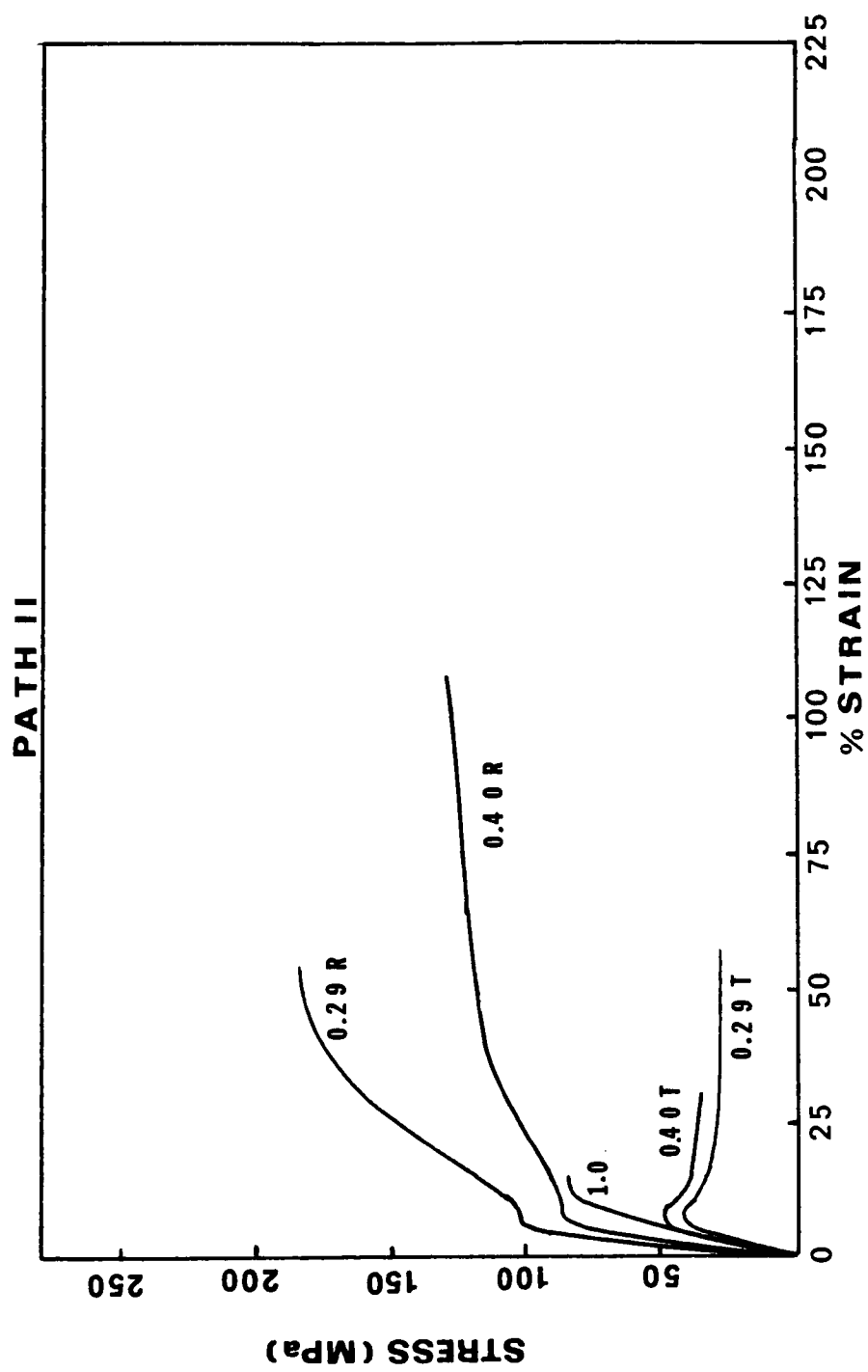


Figure 4E-4. Stress-strain curves for Path II samples.

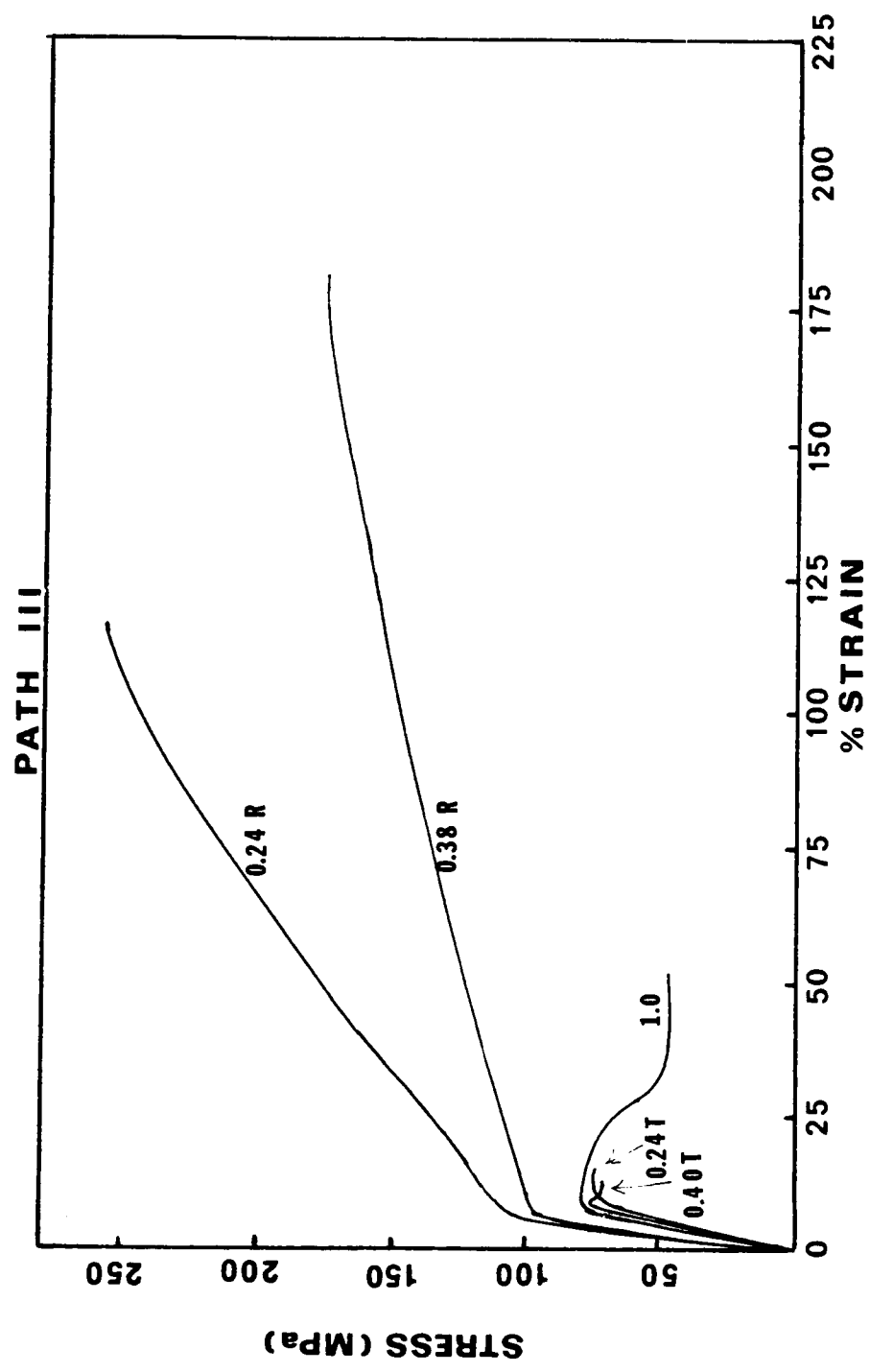


Figure 4E-5. Stress-strain curves for Path III samples.

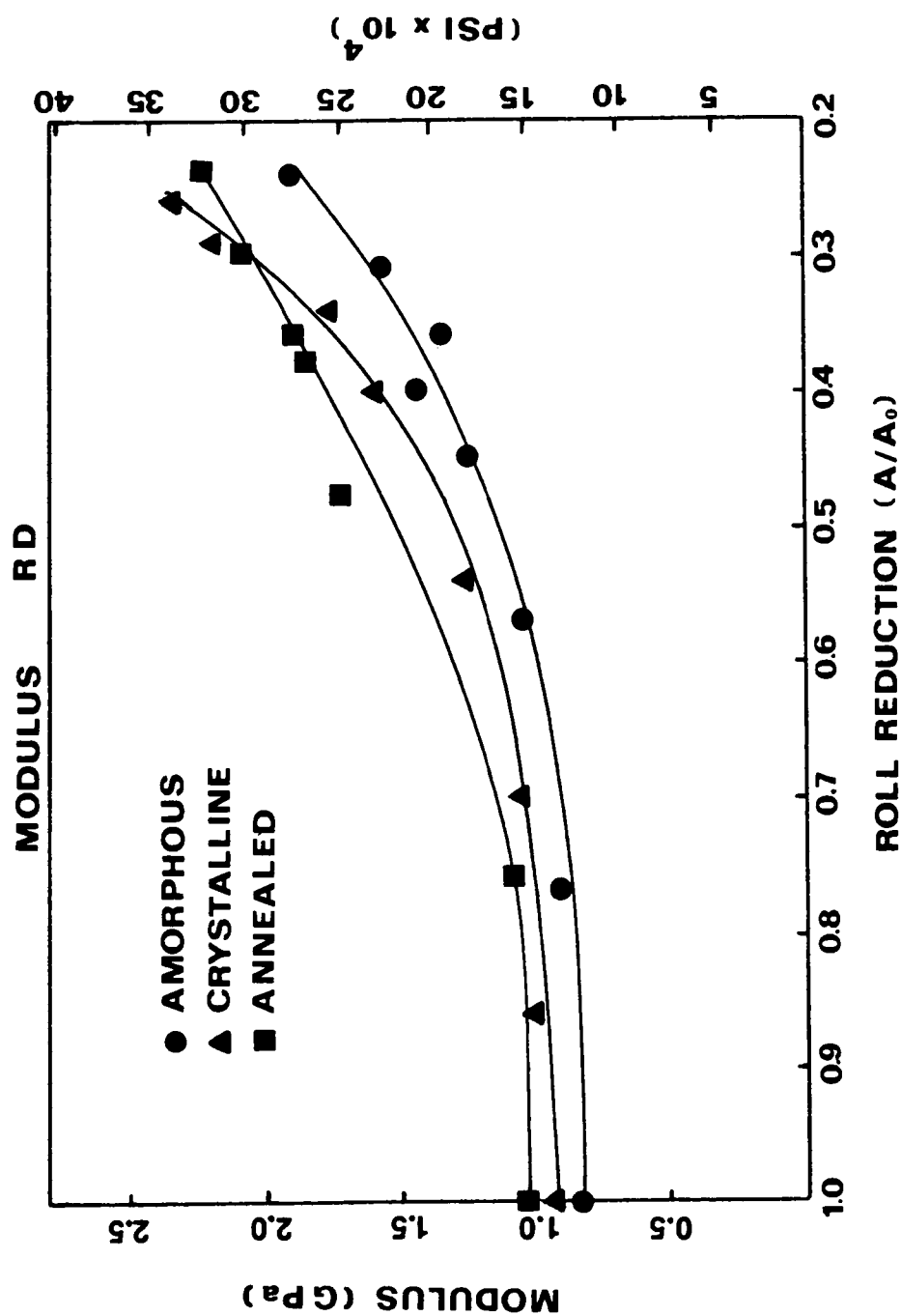


Figure 4E-6. Modulus in the RD as a function of roll reduction.

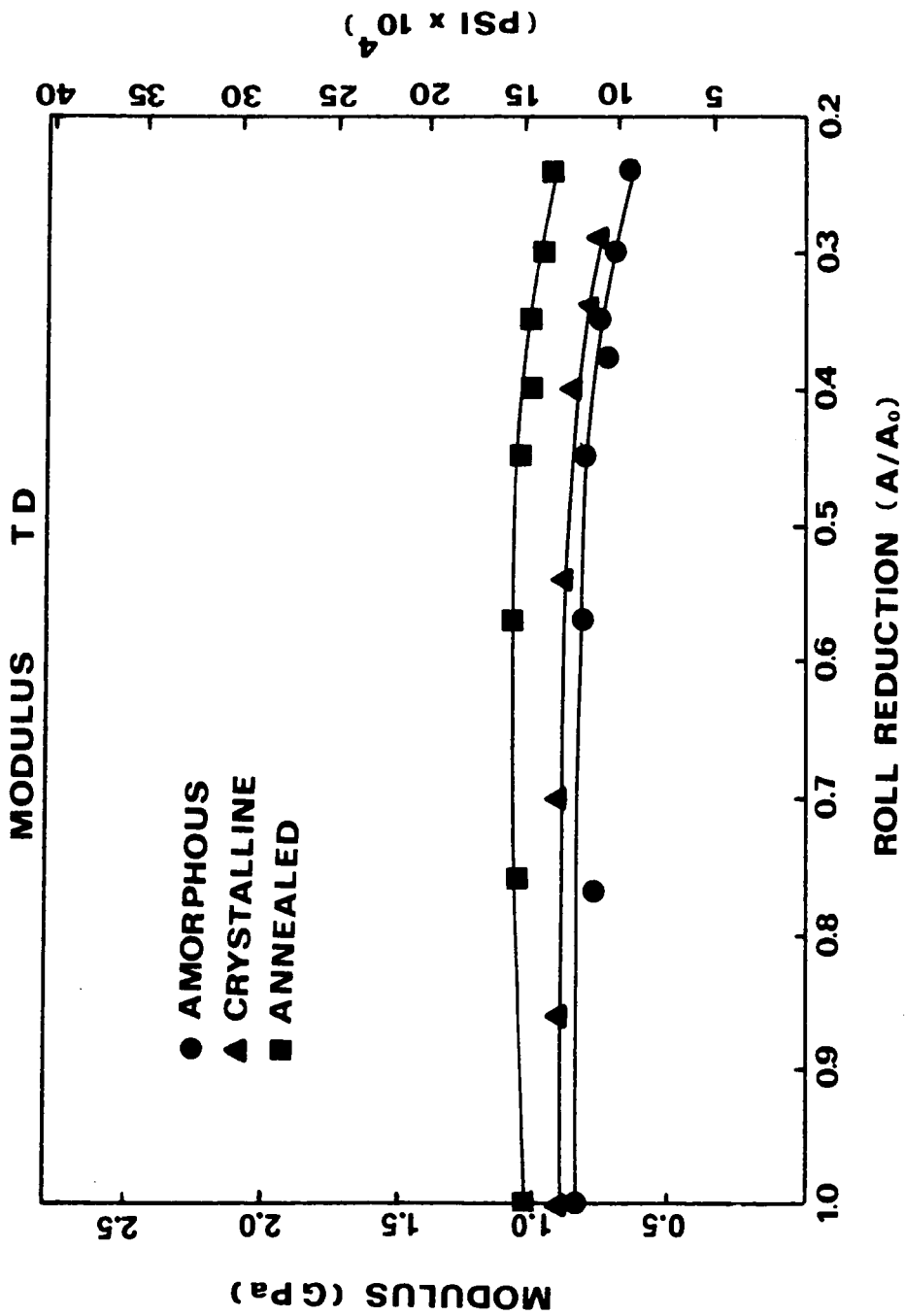


Figure 4E-7. Modulus in the TD as a function of roll reduction.

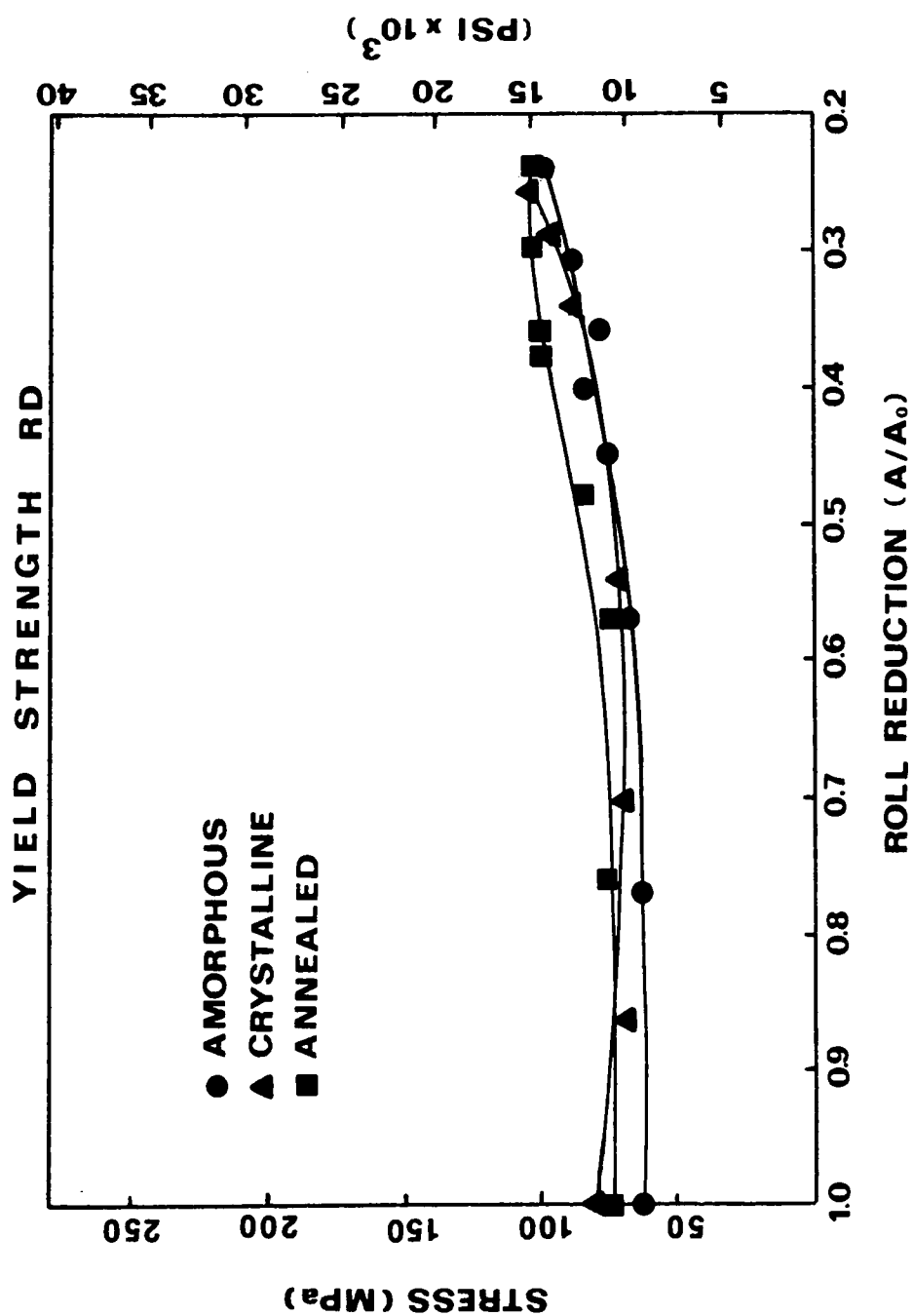


Figure 4E-8. Yield strength in the RD.

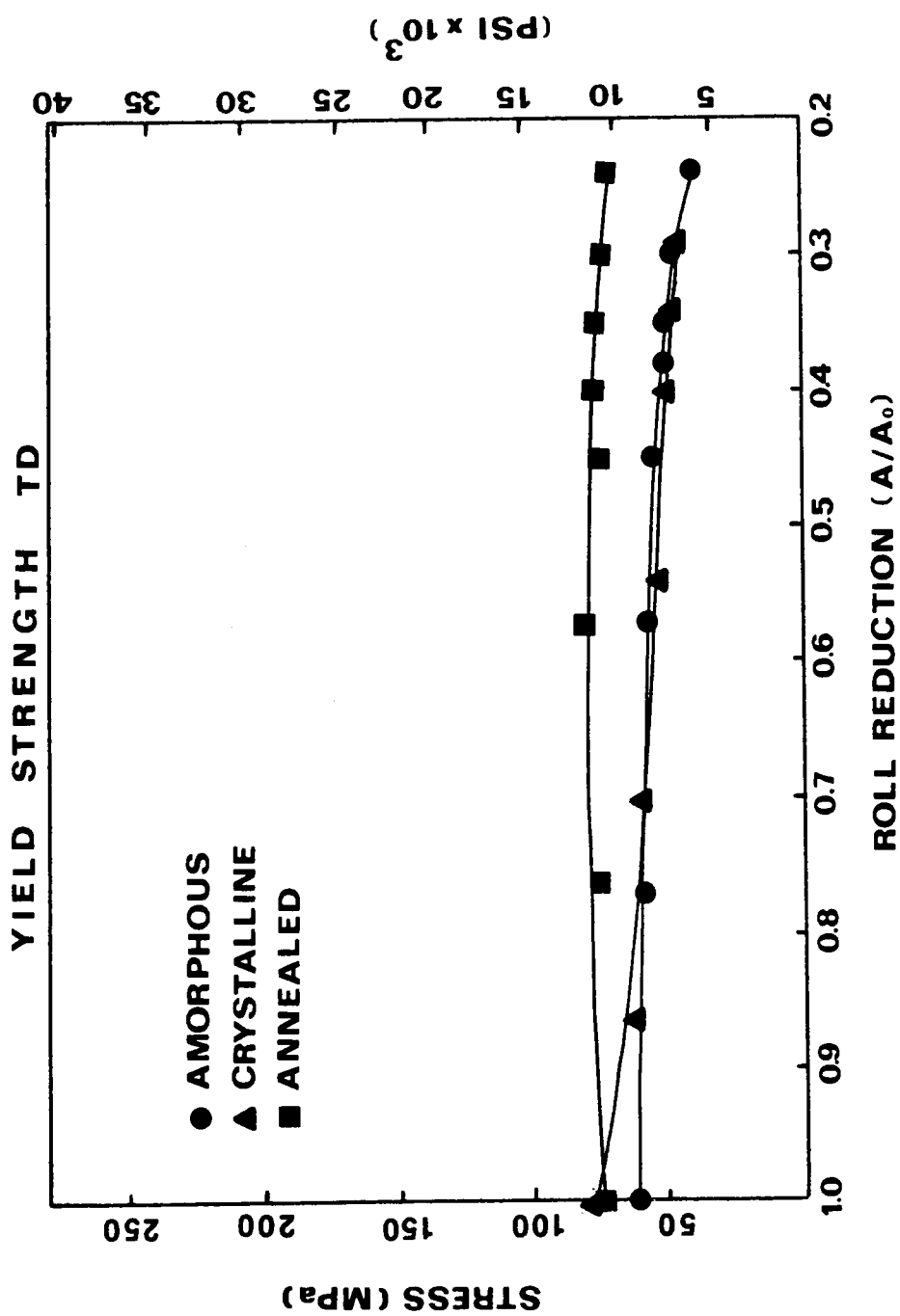


Figure 4E-9. Yield strength in the TD.

The yield strength in the TD dropped slightly with rolling. Again, the Path III samples, in general, showed the greatest strength at yield. At $A/A_0 = 0.57$, however, the Path III samples broke short and the value plotted is the same as the ultimate tensile strength.

3. Ultimate Strength

The ultimate tensile strengths in the roll and transverse directions are shown in Figures 4E-10 and 4E-11 as a function of the roll reduction.

The tensile strength in the RD increased greatly with rolling for the three paths. At the higher reductions ($A/A_0 < 0.50$), the Path III samples were the strongest, then the Path II samples.

In the transverse direction, the tensile strength tended to decrease slightly with rolling. Path III samples were strongest, with Path I and II samples showing about the same strength after initial rolling.

4. Elongation to Break

The elongations at break in the roll and transverse directions are shown as a function of the roll reduction in Figures 4E-12 and 4E-13.

The elongation at break dropped steadily in the RD for Path I samples. The elongation at break in the RD for Paths II and III was relatively low at low to moderate reductions ($A/A_0 > 0.55$). Then the elongation increases sharply at moderate reductions ($A/A_0 < 0.60$) for Path III and to a lesser extent for Path II before beginning a steady decline. Maximum elongations were observed at $A/A_0 = 0.38$ and 0.48 for Paths II and III respectively. The sudden increase in elongation is

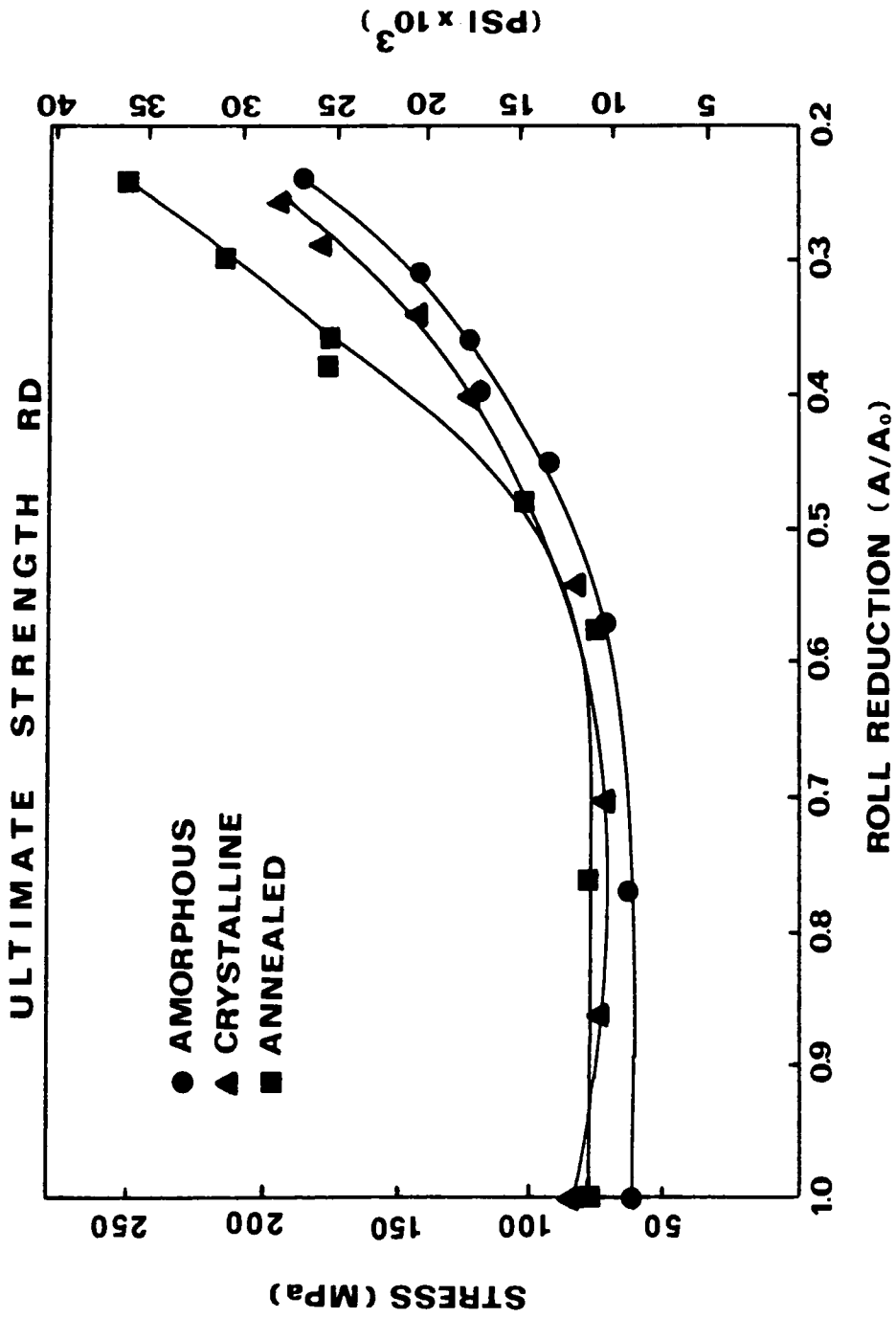


Figure 4E-10. Ultimate strength in the RD.

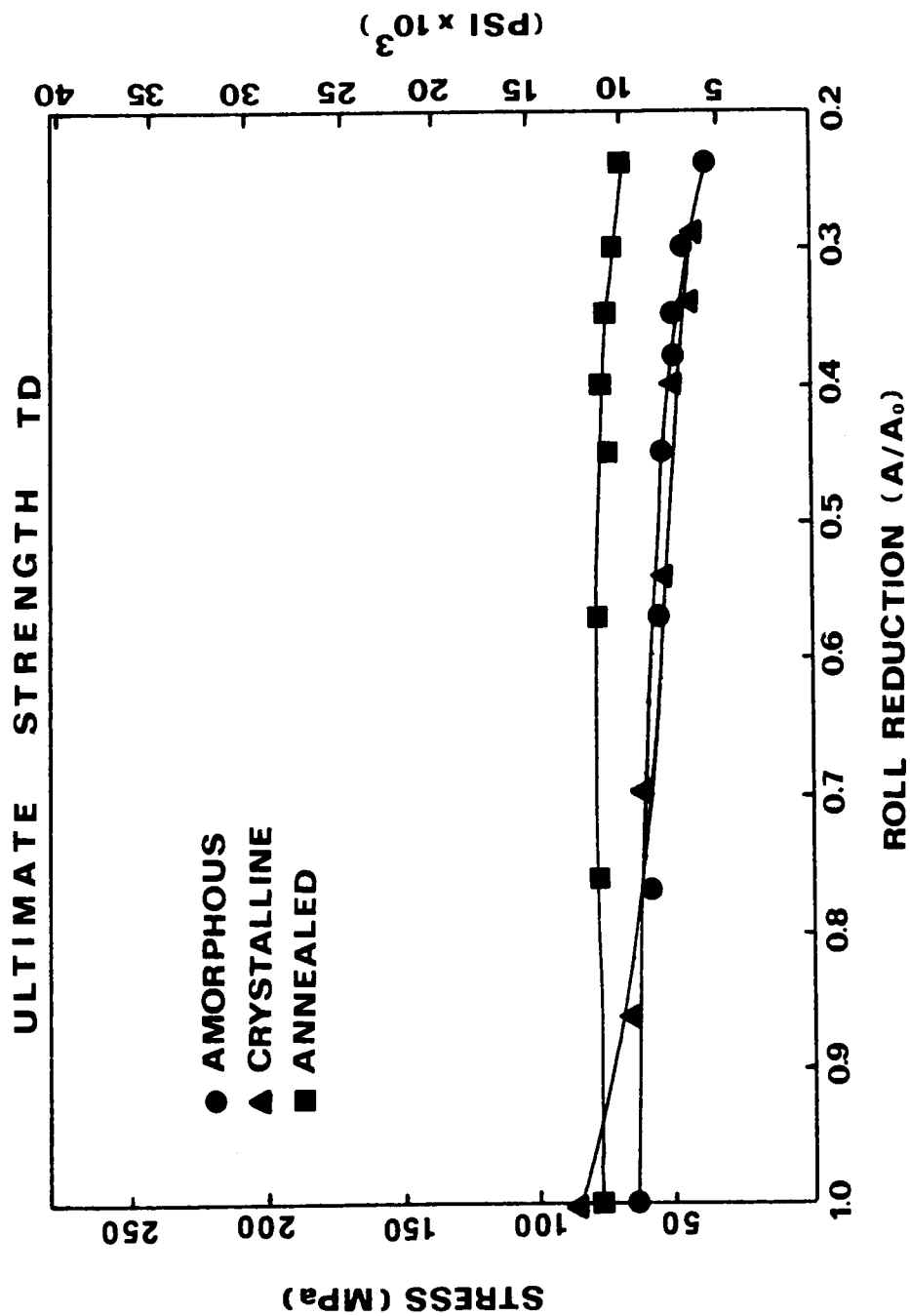


Figure 4E-11. Ultimate strength in the TD.

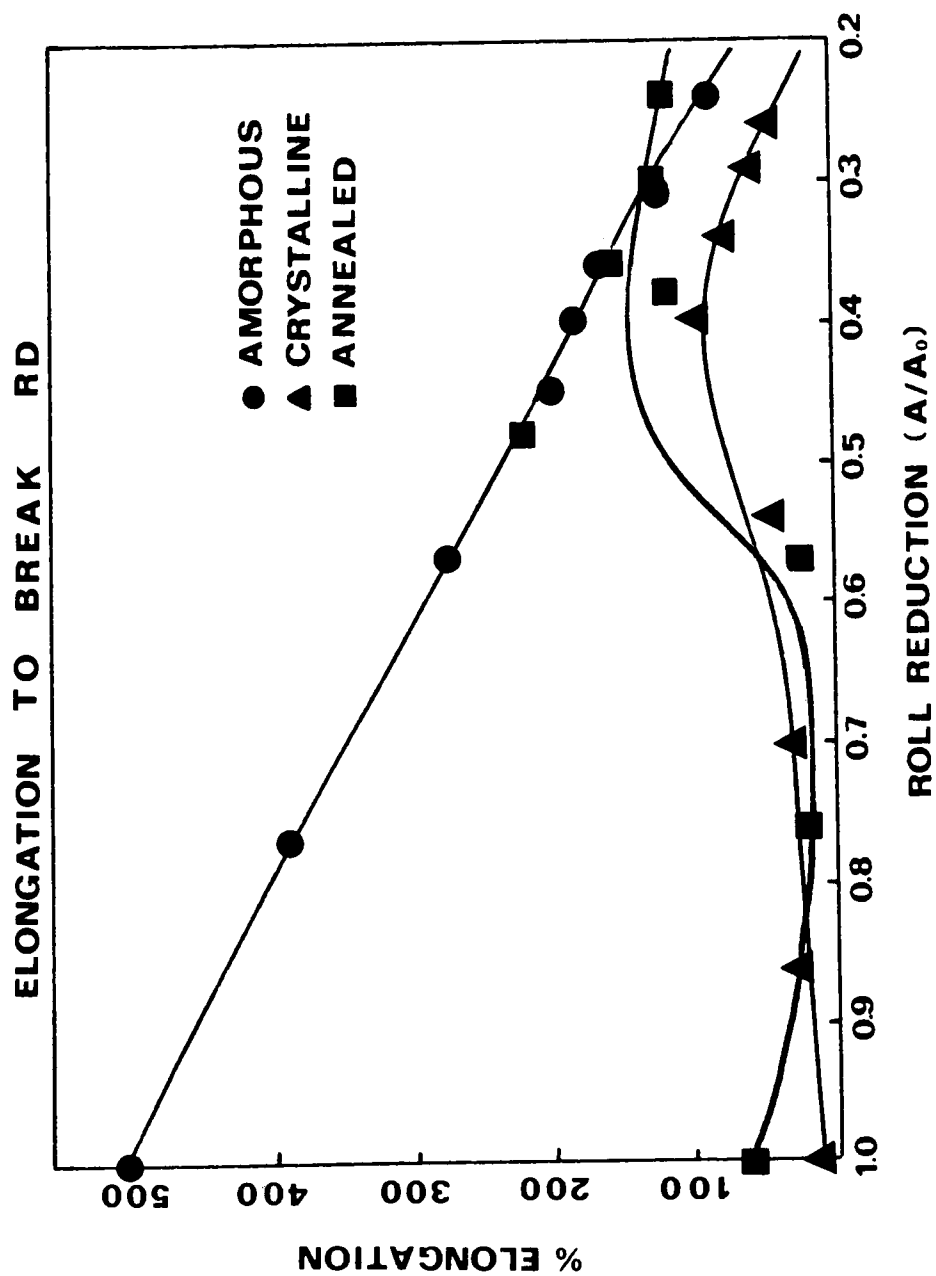


Figure 4E-12. Elongation to break in the roll direction as a function of roll reduction.

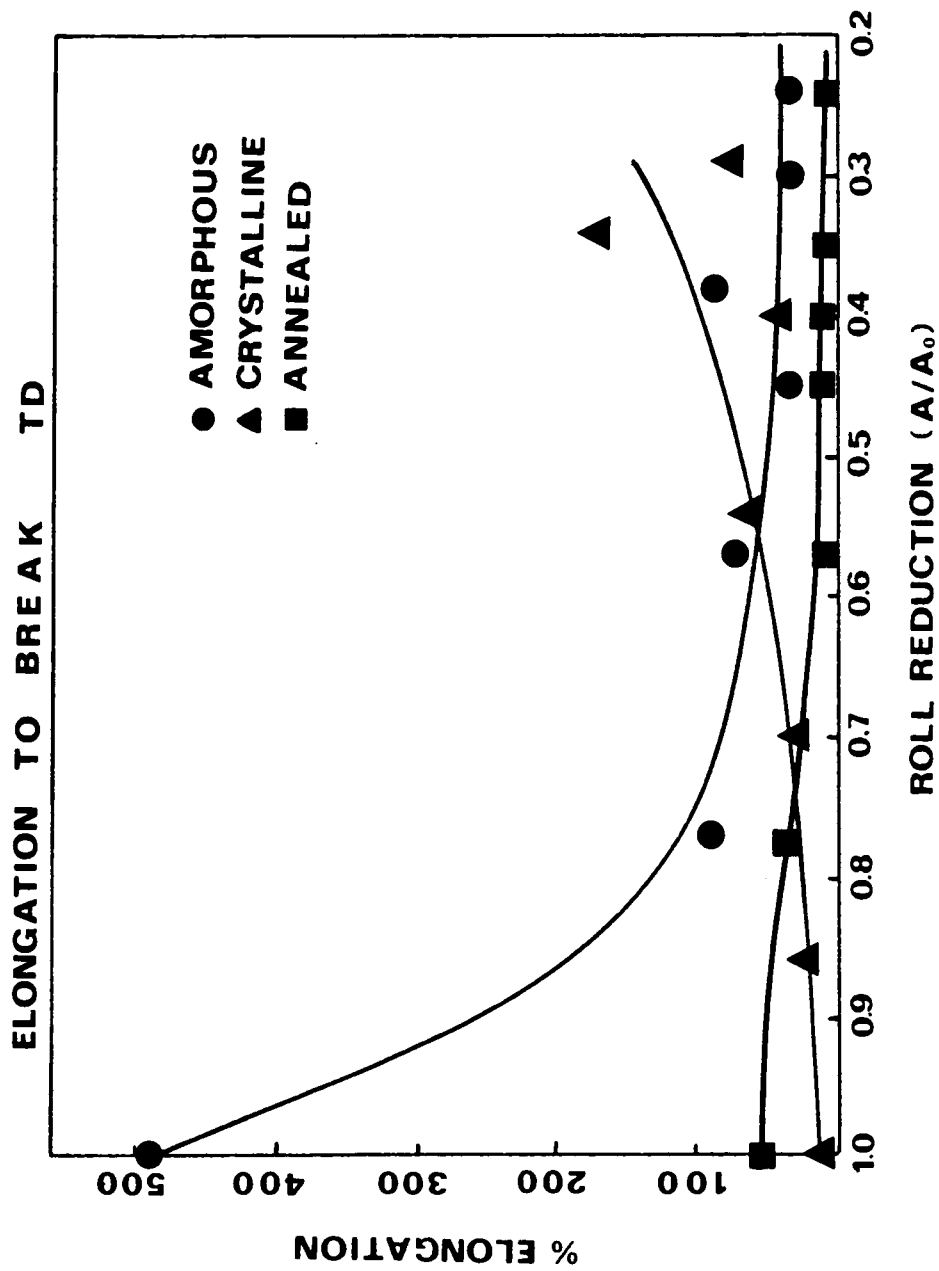


Figure 4E-13. Elongation to break in the transverse direction as a function of roll reduction.

associated with the change from a brittle to ductile type break.

In the transverse direction, the elongation to break for Path I samples dropped sharply upon initial rolling (to $A/A_0 = 0.77$). The elongation to break was not very consistent among samples of the same roll reduction but seemed to show an overall trend to decrease with rolling.

Path II samples showed a gradual increase in elongation with increasing reductions.

The elongation to break in Path III samples decreased with rolling down to $A/A_0 = 0.57$ and then remained almost constant at about 10% for higher reductions.

The low elongations observed in Paths II and III are associated with high crystallinity and a relatively brittle nature.

Discussion of Mechanical Properties

1. Path I (Amorphous)

The stress at yield in the RD increased gradually with rolling while the modulus and stress at break showed large increases. Both the elongation at yield and at failure decreased in the RD with rolling.

In the TD, the modulus, stress at yield, and stress at break all showed a slight decrease with increasing roll reductions. The elongation at yield and at break also decreased slightly with rolling.

These changes in mechanical properties can be explained in terms of the morphology. The chains become increasingly aligned in the RD as the roll reduction increases. For samples cut with the tensile axis in the RD, one would expect the modulus, yield strength, and tensile

strength to improve with rolling, since the tensile properties will be greater parallel to the chain axes than perpendicular to them. By the same reasoning, the mechanical properties in the TD would be expected to decrease.

Since the chains are partially extended and aligned in the RD during rolling, less opportunity is left for further extension during tensile testing. Hence the elongation observed during tensile testing decreases as the strain already present in the sample due to rolling increases.

The reason for the decrease in elongation to break in the TD is unclear. Perhaps as the chains become more oriented in the roll direction there are simply less chains left to hold the material together in the TD.

It is of interest to compare these results with those of others who have rolled or stretched amorphous PET films at room temperature. Gezovich and Geil (29) have published stress-strain curves for rolled PET films. Approximate values of the tensile strength and elongation to break are shown in Table 4E-1. Our values for the tensile strengths are similar to theirs, but the elongations to break are different, especially in the TD where our samples break at much lower elongations. This discrepancy could be due to flaws in the tensile bar which would make the samples break prematurely.

The results of Heffelfinger and Schmidt (34) for stretched PET films were given in Table 2C-1 (page 32). At the same approximate deformations, their values for the modulus were from 2 to 5 times greater than ours (refer to Appendix C). Tensile strengths in the mill

TABLE 4E-1
MECHANICAL PROPERTIES OF COLD-ROLLED AMORPHOUS PET

Data of Gezovich and Geil (29)				
t/t ₀	Approximate Tensile Strength (psi)		Approximate % Elongation to Break	
	RD	TD	RD	TD
0.44	12,000	5,000	100	300
0.30	18,000	7,000	50	350
Present Data				
t/t ₀	Tensile Strength (psi)		Elongation to Break %	
	RD	TD	RD	TD
0.45	13,300	7,000	200	35
0.30	20,400	6,700	120	33

direction (MD) for the stretched samples were nearly twice as great as for rolled samples, but in the TD the values were about the same as those obtained in this investigation and by Gezovich and Geil.

Both drawn and rolled samples show a strong increase in the modulus and tensile strength in RD with increasing deformation. In the TD, the modulus and tensile strength decrease with increasing reduction in the rolled samples while they first decrease and then increase with increased stretching in the drawn samples.

Elongations to break for the stretched films were less than the rolled samples in the MD, but were much greater in the TD.

Apparently, there are differences in the two deformation mechanisms which are not easily understood. There may be significant differences in the actual level of orientation achieved by these two modes of deformation. In addition, the levels of crystallinity developed may be quite different.

The apparent differences in mechanical properties may also be due in part to differences in tensile testing techniques. Heffelfinger et al. (34) do not say whether they use a "dumbbell" shape or a straight strip of film for their test samples. They do report that modulus was measured at 1% strain at an elongation rate of 100%/min. The strain rate for the present work was about 50%/min. The higher strain rate and use of a straight strip of film for the test samples would yield higher values for the modulus.

2. Path II (Crystalline)

The modulus improved greatly with rolling in the RD but decreased somewhat in the TD. The tensile strength improved markedly with rolling in the RD (as it did for Paths I and II) but decreased almost linearly with roll reduction in the TD (in contrast to Path I which showed only a slight decrease at high reductions and Path III which showed a slight improvement at high reductions).

The yield strength showed a mild increase in the RD accompanied by a slight decrease in the TD.

The tensile properties behaved as expected. One would expect improvements in the RD due to the increased number of chains aligned in the RD. The decreases in the TD would be expected since decreasing numbers of chains are aligned in this direction.

The Path II samples tended to be very brittle before rolling. Ductility improved somewhat after rolling. The elongation to break improved moderately in the RD with rolling up to $A/A_0 = 0.40$. Further rolling reduced the elongation observed during tensile testing. Apparently ductility is improved as the spherulites are broken up but decreases as the chains become more extended at the high reductions.

In contrast to Paths I and III, the elongation to break increased with rolling in the TD as well, falling off only at the highest reduction. The ductility seems to improve due to the fragmentation of the spherulites, but as the chains become highly oriented in the RD the elongation drops in the TD simply because there are fewer chains left holding the samples together in the TD.

3. Path III (Rolled and Annealed)

The modulus increased greatly in the RD, while decreasing slightly in the TD.

The stress at yield showed modest improvements in the RD with rolling but decreased slightly at high reductions in the TD.

The tensile strength improved greatly in the RD with rolling, but showed only a slight increase in the TD.

The elongation at yield dropped in the RD with rolling. In the TD, erratic results were obtained but an overall decrease was noted.

In the unrolled samples, about a 50% elongation occurs with a ductile failure. The elongation to break decreases with rolling in the RD to $A/A_0 = 0.57$ and mostly brittle fractures are observed. At higher reductions necking occurs, the elongation to break jumps up greatly (remaining above 100%), and ductile failures are observed.

In the TD, the elongation to break drops dramatically from about 50% in the unrolled case to less than 10% at reductions greater than $A/A_0 = 0.57$. A ductile break is observed at low reductions. This changes to a brittle break at $A/A_0 = 0.57$. Short necks were observed in the unrolled and lightly rolled samples, but the samples broke before the neck could propagate very far.

These changes can be explained in terms of the chain orientation.

The modulus, yield, strength, and tensile strength would all be expected to increase in the RD as the chains become more aligned in the RD.

Tensile properties in the TD would be expected to decrease as chains become oriented in the RD. The modulus and yield stress

show slight decreases, but the tensile strength actually shows a slight increase. (This is interesting in view of the decrease in elongation to break and a change from a ductile to brittle failure.)

The unrolled and moderately rolled samples are rather brittle and relatively low elongations to break are observed in both the RD and TD compared to unannealed samples. The polymer chains are tied up in crystalline structures and very little slippage can occur. The samples break before the chains can elongate.

At high reductions ($A/A_0 < 0.57$), some morphological change occurs and the samples become tougher in the RD and weaker in the TD. Longer elongations to break occur in the RD due to necking, but samples split easily when stretched in the TD.

Pole figures show the orientation of the chains in the RD suddenly increases between $A/A_0 = 0.57$ and $A/A_0 = 0.40$ and that the (100) planes become preferentially aligned in the plane of the film.

Apparently, the alignment of the chains in the RD makes the sample stronger in this direction and reduces the tendency for it to break. Elongations are achieved which are comparable to those of Path I samples.

The low elongations observed in the TD at reductions greater than $A/A_0 = 0.57$ are probably due to the lack of molecules oriented in the TD. The chains just pull apart.

Since no mechanical property data was obtained for Path IV (Hot Rolling), the data of Lundsager (48) and Dunnington et al. (23) for hot rolling of semicrystalline PET films will be compared to Path II (Crystalline) and Path III (Rolled and Annealed) results (see Table 4E-2).

A much higher modulus was obtained by hot rolling than by either

TABLE 4E-2
MECHANICAL PROPERTIES OF HOT ROLLED PET FILMS

t/t_0	Tensile Strength (psi)		Young's Modulus (psi)		% Elongation to Break	
	RD	TD	RD	TD	RD	TD
0.40 ¹	25,600	7,200	820,000	340,000	68	32
0.32 ²	37,900	7,880				
0.26 ²	46,500	7,790				
0.23 ²	54,800	7,100				
0.21 ²	58,200	6,800				
0.20 ²	51,900	8,200				

¹Data of Lundsager (48)
Initial Density: 1.37 gm/cm³
Rolls were heated to 160°C
Initial film thickness: 8 mils

²Data of Dunnington et al₀ (23)
Films were heated to 150°C
Initial film thickness: 7 mils

Path II or Path III. Higher tensile strengths were obtained in the RD for hot rolled samples than for Paths II and III, while just the reverse is true in the TD.

Apparently, hot rolling imparts a greater degree of strength in the RD for a given roll reduction than either cold rolling of a crystalline film (Path II) or cold rolling of amorphous film followed by annealing (Path III).

CHAPTER V

RESULTS AND DISCUSSION: PATH IV

In this path an attempt was made to simultaneously roll and crystallize PET films. Samples were heated in an air oven to the desired temperature and then quickly passed through the rolls.

Actual oven temperatures used for this path turned out to be 80° , 97° , 115° , 120° , and 130°C .

As discussed in the experimental section several problems plagued this experiment making the results difficult to interpret.

Figure 5-1 shows a plot of density as a function of roll reduction at the five different initial temperatures. The actual temperature of the sample was difficult to ascertain due to various cooling effects. Only the initial temperature before rolling is known.

As can be seen from the graph the samples tended either to crystallize in the oven before rolling (at 120° and 130°) or remain almost amorphous (80° , 97° , and 115°). At 115°C the most highly rolled sample appears to crystallize, but this can be traced to the high temperature generated by the rapid rolling process.

At the three lowest temperatures the samples appear to behave like the Path I samples - a slight increase in density occurs at the highest roll reductions.

At the two higher temperatures the sample behaved similar to Path II samples. The samples are somewhat crystalline before rolling. As they are rolled, the density decreases, probably as a result of crushing crystallites. At high reductions, however, the trend is

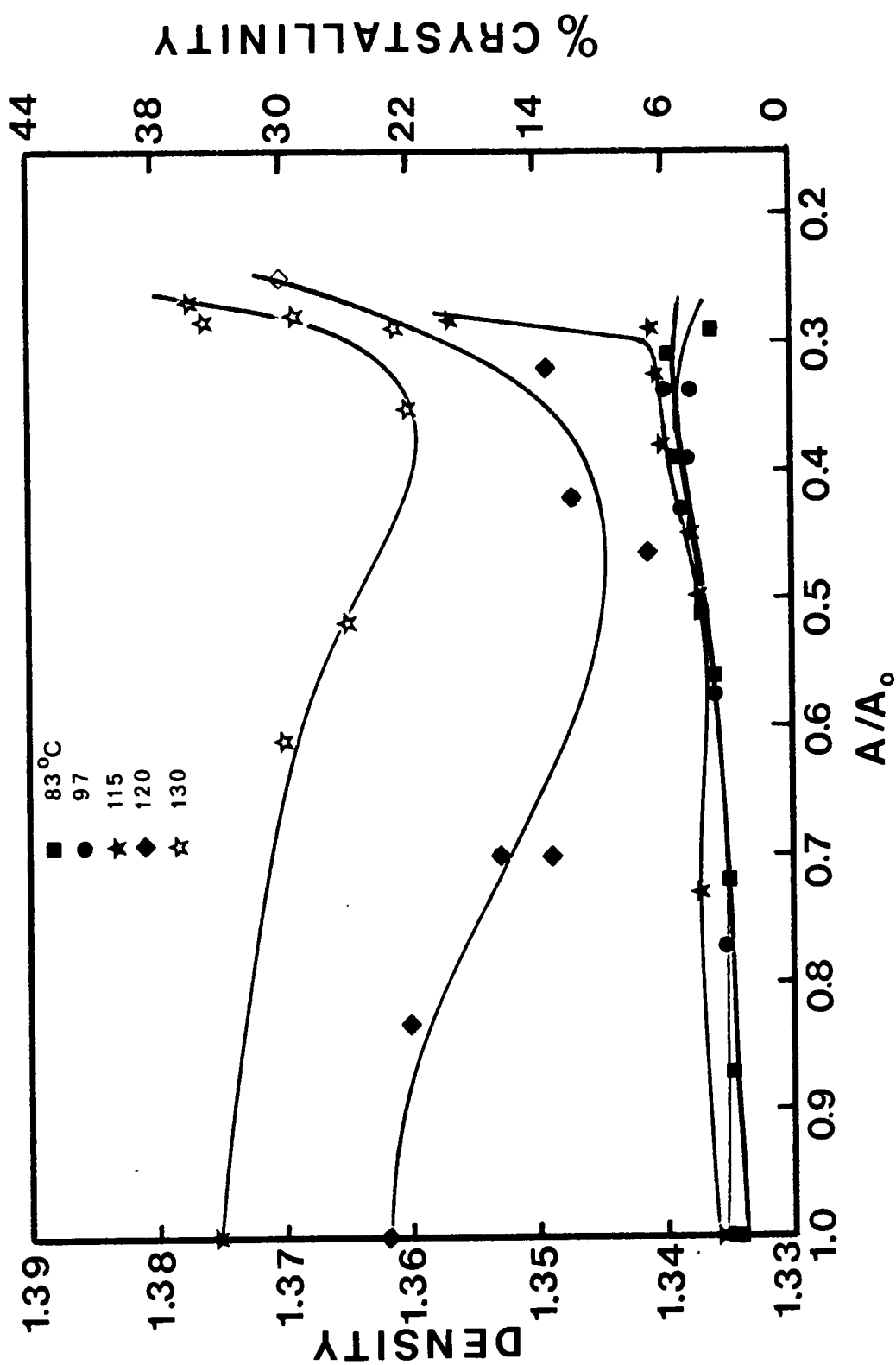


Figure 5-1. Density as a function of roll reduction and temperature for hot rolled samples.

reversed. The density begins to increase. Probably, the combination of high orientation, the high initial temperatures, and the heat generated by rapid reduction causes additional crystallization to occur.

It was difficult to find conditions in which the sample gradually increased in crystallinity with increased rolling. Large reductions with a single pass were impossible due to the rubbery nature of the sample and the accompanying difficulty of pushing the sample into the rolls. Hence, the samples cooled significantly during the time it took to achieve a particular reduction. If the sample were placed back in the oven to reheat, the orientation would be lost and eventually the sample would crystallize due only to annealing effects.

On the other hand, at the higher temperatures, the samples were partially crystalline to begin with. These were easier to roll since they were stiff enough to push into the rolls and they retained the orientation imparted by rolling. Hence, a high level of crystallinity could be achieved with these samples.

Satisfactory results could not be obtained under any of the Path IV processing conditions used in this experiment. The many problems encountered with this method make quantitative results impossible, so further work in this area was discontinued.

Although Dhingra (15) obtained good results with this method for polypropylene, the results obtained here suggest that this method is inappropriate for PET due to the rubbery and brittle states encountered at different times during the process. Perhaps a better method is that of rolling semicrystalline films between heated rolls (150° - 190° C) using techniques reported in the literature (23,48).

CHAPTER VI

SUMMARY AND CONCLUSIONS

A. MORPHOLOGY OF PATH I, II, AND III SAMPLES

WAXD patterns and pole figures indicate the chains in Path I samples become preferentially oriented parallel to the RD during rolling. As the chains become more oriented the morphology changes from the initial amorphous structure to a somewhat more ordered paracrystalline structure which increases in degree of order with increases in roll reduction. Small crystallites are believed to form at the highest reductions. DSC results indicate an increase in crystallinity of about 30%. It should be noted that this occurs during rolling under ambient conditions which are well below the glass transition temperature of PET. However, it is not clear to what extent the PET sample heats up during rolling due to the mechanical deformation imposed.

In Path II, the samples are highly crystalline and spherulitic before rolling. During rolling the spherulites are crushed and the lamellae become tilted toward the TD. At the highest reductions, the lamellae themselves are crushed and the chains become preferentially aligned parallel to the RD. The crystallinity remains almost constant during rolling, but density results indicate voids are formed.

Path III is more complicated. In this case some line nuclei are believed to form in the samples during rolling. These are a part of the strain-induced changes in structure noted for Path I samples. Upon annealing these line nuclei give rise to cylindrites. The higher

the reduction, the greater the number of line nuclei formed. Competition for space eventually limits the size of the cylindrites so that the greater the number of nuclei the smaller the cylindrites. At high reductions the chains are preferentially oriented in the RD and the benzene rings in the chains tend to align parallel to the plane of the films. Path III samples achieve a much higher level of crystallite orientation and chain alignment than Path II samples, as indicated by the pole figures.

Perhaps the most interesting thing about Path II and III samples is that both paths give rise to four point SAXS patterns but from two entirely different morphologies produced by two different mechanisms.

In Path II, the crystalline structure is present before rolling. Rolling crushes spherulites and tilts the lamellae toward the RD. The resulting chevron shaped structure is believed responsible for the four point pattern seen when the x-ray beam is parallel to TD. These effects are similar to those found by Dhingra et al. (16) for the rolling of crystalline isotactic polypropylene, and by Gesovich and Geil (28) for crystalline polyoxymethylene. Thus such features would appear to be rather general for the rolling of semicrystalline polymers.

In Path III, the samples are highly oriented before crystallization takes place. The cylindrites formed during annealing are believed to produce four point patterns because of the "checkerboard" effect created when the amorphous region of one cylindrite is next to the crystalline region of an adjacent cylindrite. Thus, an entirely different texture produces the four point pattern in rolled and subsequent annealed PET.

While both morphologies developed by Path II and by Path III

produce four point patterns when the x-ray beam is parallel to the TD, the detailed appearance of these patterns is different. In Path II, the patterns are rather cross-shaped and the lobes are distinctly separated. In Path III, the patterns are more elliptical shaped and the lobes are not distinctly separated except at the highest reductions.

B. MECHANICAL PROPERTIES OF PATH I, II, AND III SAMPLES

As shown by pole figures, Path III samples achieve a higher degree of order and alignment than either Path I or II samples. The annealing treatment also increases their crystallinities above the level attained in the other two paths. As a result, Path III samples, in general, have a higher modulus, yield strength, and ultimate tensile strength in both the roll and transverse directions than either Path I or II samples. Path II samples do, however, have a slightly higher modulus in the RD at very high reductions ($A/A_0 < 0.30$). It is also possible that Path II samples might develop higher modulus and strength properties than Path III samples if they were rolled at elevated temperatures as suggested by the patents of Dunnington et al. (23) and Lundsager (48). This possibility was not tested in this research.

Path II samples have a slightly higher modulus than Path I samples at all reduction levels in both the roll and transverse directions. This is presumably due to the importance of crystalline regions in stabilizing chains and tying them together as physical crosslinks.

Interestingly enough, the yield strengths and ultimate strengths are very similar for Paths I and II in both the roll and transverse directions for all but the unrolled case.

The elongation to break tended to be greater in both the roll and transverse directions for the amorphous Path I samples than for the crystalline samples of Paths II and III except at high reductions. Path III samples had low elongations to break and tended to be brittle at low reductions. At reductions greater than that corresponding to $A/A_0 = 0.57$, the Path III samples became tough and exhibited a ductile break when tested in the RD. As a result, higher elongations were achieved at the higher reduction levels. The maximum elongation was reached at $A/A_0 = 0.48$. Samples tested in the transverse direction had low elongations to break ($< 10\%$) and exhibited a brittle fracture at A/A_0 less than 0.70. Path II samples were also brittle at low reductions but ductility improved with rolling up to a point. Maximum elongations were obtained at A/A_0 around 0.35 to 0.40 in both the roll and transverse directions. The increase with rolling in the ductility of Path II samples can probably be attributed to the break-up of the spherulites during rolling. A similar phenomenon has been observed by Dhingra et al. (16) for isotactic polypropylene.

C. COMPARISON OF AMORPHOUS AND CRYSTALLINE PATHS

One of the objectives of this research was to make a direct comparison of a rolled crystalline polymer to a rolled amorphous polymer. The following conclusions can be drawn for PET.

- 1) Crystallinity increases with rolling for amorphous PET due to "strain-induced crystallization." Crystallinity remains relatively constant during rolling of crystalline samples.
- 2) The density of amorphous PET increases during rolling while it

decreases for crystalline samples. The decrease has been attributed to the break-up of spherulites and void formation.

3) Rolling imparts ductility to crystalline PET due to the break-up of spherulitic structures. Rolling reduces the elongation to break in amorphous PET, although elongations are much higher initially than for crystalline samples. The decrease in the roll direction is due to the orientation imparted to the sample, while the decrease in the transverse direction is due to the increased fibrillar nature of the sample at higher reductions.

4) The modulus is greater in both the roll and transverse directions at all reductions for crystalline PET than for rolled amorphous samples. This is due both to the rigidity of the crystalline structure and to the physical entanglements of the tie molecule chain ends in the crystallites. Yield strengths are surprisingly similar in both directions and at all reductions. The ultimate strengths are slightly higher in the RD for the crystalline samples but are almost identical in the TD.

D. RECOMMENDATIONS

The attempt to roll and simultaneously crystallize PET (Path IV) was unsuccessful. In this research, the polymer was first heated and then passed through rolls at about 40°C. As discussed in Chapter V there were many problems with this particular method. Perhaps a better way to roll and crystallize simultaneously would be to pass partially crystallized polymer through hot rolls (150° to 190°C) as suggested by two patents (23, 48). Another way would be to make reductions large

enough and fast enough to substantially heat the polymer as it passes through the rolls.

Perhaps more attention should be given to the hot rolling of highly crystalline PET. Recent work (7) on polyolefins indicates that higher modulus and tensile strength can be achieved by rolling at elevated temperature. Some work in the patent literature suggest that this might be feasible for polyester also (23, 48).

Another area of research which looks interesting is biaxial rolling of PET. Two samples were cross-rolled to moderate and high reductions. The highly rolled sample was very tough in all directions in contrast to the highly rolled uniaxial samples which tended to fibrillate. Also, larger final reductions could be obtained by cross-rolling without destroying the sample.

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APPENDICES

APPENDIX A

CALCULATION OF MECHANICAL PROPERTIES

Gage Length $L_0 = 0.345" = 9.53 \text{ mm}$.

Cross Head Speed CHS = 0.2"/min

Elongation $(L-L_0) = (\text{CHS} \cdot D)/\text{CS}$

where L is the elongation plus the gage length, D is the distance the chart paper had moved at a particular point during that test, and CS is the chart speed.

For example,

$$L-L_0 = \frac{(0.02"/\text{min}) \cdot (5 \text{ in})}{(50 \text{ in}/\text{min})} = 0.002"$$

Strain γ is defined as $(L-L_0)/L_0$.

Modulus E was calculated as follows:

$$E = \lim_{\gamma \rightarrow 0} \frac{F/A_0}{\gamma} \quad (\text{tangent modulus}) \quad (\text{A.1})$$

where F is the load measured at a particular strain.

Engineering stress σ at any given point was calculated by the following equation.

$$\sigma = \frac{F}{A_0} \quad (\text{A.2})$$

APPENDIX B

TABLE B-1

MECHANICAL PROPERTIES IN THE ROLL DIRECTION

	A/A_0	Modulus (MPa)	Yield Stress (MPa)	Elongation to Break (%)	Breaking Stress (MPa)	Ultimate Strength (MPa)
Path I						
1	1.00	795	61	507	40	61
2	0.77	867	62	387	50	62
3	0.57	990	67	273	71	71
4	0.45	1202	75	199	92	92
5	0.40	1390	83	182	121	121
6	0.36	1295	77	159	123	123
7	0.31	1533	88	121	141	141
8	0.24	1862	97	85	185	185
Path II						
1	1.00	910	80	14	84	84
2	0.86	970	67	24	73	73
3	0.70	1013	68	27	71	71
4	0.54	1217	70	40	81	81
5	0.40	1539	81	96	119	119
6	0.34	1713	87	74	141	141
7	0.29	2134	95	55	177	177
8	0.26	2280	102	43	194	194
Path III						
1	1.00	996	73	59	48	78
2	0.76	1035	75	17	75	77
3	0.57	948	73	22	69	73
4	0.48	1687	83	220	101	101
5	0.38	1815	98	117	176	176
6	0.36	1848	99	162	174	174
7	0.30	2027	102	125	212	212
8	0.24	2181	102	117	249	249

TABLE B-2
MECHANICAL PROPERTIES IN THE TRANSVERSE DIRECTION

	A/A_0	Modulus (MPa)	Yield Stress (MPa)	Elongation to Break (%)	Breaking Stress (MPa)	Ultimate Strength (MPa)
Path I						
1	1.00	843	62	232	32	62
2	0.77	777	59	88	29	59
3	0.57	814	55	74	28	55
4	0.45	798	53	35	29	53
5	0.38	717	49	89	26	49
6	0.35	735	49	45	26	49
7	0.30	689	46	33	24	46
8	0.24	627	38	35	17	38
Path II						
1	1.00	910	80	14	84	84
2	0.86	902	62	23	63	63
3	0.70	902	59	28	54	59
4	0.54	874	52	68	37	52
5	0.40	842	48	39	35	48
6	0.34	773	46	173	32	46
7	0.29	734	43	76	28	43
8	0.26	-	-	-	-	-
Path III						
1	1.00	1039	74	51	47	75
2	0.76	1053	75	40	46	76
3	0.57	1073	77	9	77	77
4	0.45	1037	74	12	70	74
5	0.40	995	75	11	72	76
6	0.35	995	74	11	72	74
7	0.30	950	72	10	71	72
8	0.24	919	69	9	69	69

VITA

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