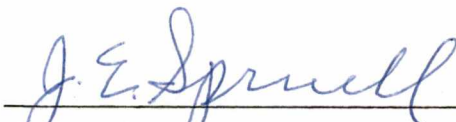


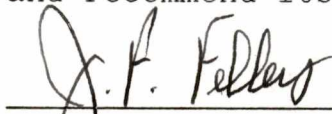
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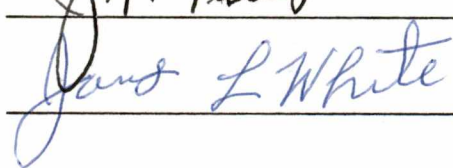
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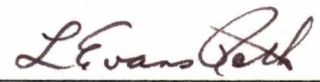
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Vice Chancellor
Graduate Studies and Research

SPIN-DRAW INTERACTION EFFECTS ON
FIBRILLATION OF POLYPROPYLENE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Hassan Bodaghi

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Above all I am grateful to my wife for her admiration, and my parents for their support and devoted love.

DEDICATION

This thesis is dedicated to my wife Trisha Bodaghi, whose enduring love and compassion has helped make this attainable. I also devote this thesis to my son, Kavous Kirk, for the warmth he brings into my life.

Also I would like to honor my parents with this thesis for all their love and encouragement.

ABSTRACT

Fibrillation is a phenomenon which arises in the processing of synthetic fibers. Fibrillation is related to a transformation from a spherulitic or cylindritic structure characteristic of the morphology of melt spun filaments to a fibrillar morphology characteristic of drawn filaments. The fibers break up into small "Fibrils" during the plastic deformation of drawing. A similar effect can occur in the processing of tapes and films and is generally detrimental to the physical and mechanical properties. Fibrillation is apparently due, at least in part, to the growth of longitudinal microvoids during deformation and transformation into the final fiber structure. The degree of fibrillation depends on many variables such as draw ratio, draw temperature, the initial structure of the spun filaments, and the molecular characteristics of the polymer. This research was undertaken in order to experimentally determine the effects of such variables on the level of fibrillation.

Various fibrillated polypropylene fibers were prepared at different spinning and drawing conditions. Hercules Profax^(R) (6323,6423) and Diamond Shamrock^(R) (5831-106-7) having a range of melt flow indices (6.6-25) were selected for experimental study. Each polymer was spun at two spinning conditions representing low and high molecular orientation in the spun filaments. These filaments were then drawn 3.5X and 6X at 25°C, 60°C, 90°C, and 150°C.

The structure of the spun and drawn filaments were characterized using scanning electron microscopy, wide angle x-ray diffraction, small angle x-ray scattering, birefringence and density measurements. Based on preliminary qualitative measurements, the small angle x-ray scattering from selected samples was measured quantitatively using the 10 meter Small Angle X-ray Scattering facility at the National Center for Small Angle Scattering at Oak Ridge, Tennessee (NCSASR). The volume fraction of microvoids was computed from the invariant of the scattered intensity, and the size, shape, and number density studied by subjecting the scattered intensity to Guinier Analysis.

The tensile mechanical properties of both as-spun and drawn filaments were measured. A series of compression molded polypropylene sheets (6423, 6323, 5831-106-7) were also drawn using an Instron tensile testing machine. Two drawing processes were examined: cold drawing at 25°C include draw ratios of 4X and 6X; hot drawing at 150°C include draw ratio of 4X and 6X. The structure and mechanical properties of the drawn sheets were also characterized.

Wide Angle X-ray Scattering (WAXS) patterns of drawn samples showed that cold drawing transformed the monoclinic form of as-melt spun filament into a more oriented but disordered structure, while hot drawing produced a highly oriented well-formed monoclinic structure. Samples drawn at

150°C showed somewhat lower level of birefringence and c-axis crystalline orientation function (f_c).

The volume fraction of microvoids computed from the Small Angle X-ray Scattering (SAXS) technique was found to correlate well with microvoid fractions estimated from a combination of crystallinity (DSC technique) and density measurements. These showed that the volume fraction of microvoids increased with; 1) increase in draw ratio, 2) decrease in draw temperature, 3) increased orientation in the as-spun filaments, and 4) increased molecular weight of the polypropylene. Volume fractions of microvoids varied from about 0.4×10^{-3} (0.04%) to about 0.28×10^{-1} (2.8%).

The Guinier analysis showed that the average void size had dimensions of $250\text{--}400 \text{ \AA}$ parallel to the fiber axis and of order $150\text{--}200 \text{ \AA}$ perpendicular to the fiber axis. Based on results of void fraction, void dimensions, void number density and Scanning Electron Microscopy (SEM) photomicrographs it was found that a) fibrillation increased with increasing draw ratio, b) drawing at 25°C is accompanied by very extensive fibrillation, while the amount of fibrillation decreases as drawing temperature increases, c) the high melt index samples showed less fibrillation than those with low melt index, and d) the filament with low take-up velocity (30 mm/min) during spinning fibrillate less comparatively than those with higher take-up.

The drawn fibers showed better mechanical properties than melt spun fibers. Under the experimental conditions investigated, the mechanical properties such as; tensile strength, tangent modulus and elongation to break of the melt spun and drawn fibers all correlated with the birefringence. It was also found that mechanical properties are mainly a function of the orientation and are not very much affected by changes in fibrillation per se.

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CHAPTER I

INTRODUCTION

Polypropylene is a very important commercial synthetic polymer. Since the range of properties in polypropylene fibers is found to be very large, studies of the processing operations used in its fabrication are of considerable interest.

Preparation of fiber generally proceeds in three stages. The polymer is first melted and extruded through a spinneret to form a small diameter filament. In this melt spinning process the molten filaments are drawn down by forces supplied by a take-up device while they are cooled and solidified. This may induce significant molecular orientation into the as-spun filaments (91,52,101,65,42,90,74) but most filaments are given increased orientation by a second processing step called drawing. Here the spun filaments are elongated in the solid state as they pass over a hot plate. The drawing process not only induces additional molecular orientation but transforms the spherulitic or cylindritic structure of the spun filament into a fibrillar morphology (74,90,99,19,111,101). In the last processing stage, the drawn fibers are frequently heat set under tension (90,65). This helps to eliminate a tendency for shrinkage when the fiber is exposed to elevated temperatures.

Fiber property variations are the result of differences in the fiber structure induced by different processing conditions. In addition to variations in elastic modulus, tenacity, elongation to break, yield strength, shrinkage and other properties, drawing processes are accompanied by fibrillation (74,90,75,52,111,73). Fibrillation is a phenomenon which arises in the processing of synthetic fibers in which the individual fibers break up into smaller fibrils and microfibrils. A similar effect may also occur in the processing of tapes and films.

Depending upon the application, fibrillation may be detrimental or desirable. In any case, there are no methods of quantitatively characterizing the degree of fibrillation resulting from a given processing history. Fibrillation is apparently due, at least in part, to the transformation to the fibrillar morphology described above. It appears that fibrillation is a consequence of growth of longitudinal voids during deformation and transformation into a final fiber structure. While this is true it does not follow that all fibers of a given polymer processed so as to have the same elastic modulus (for example) will also have the same degree of fibrillation. A given property value such as the modulus can be achieved via several different processing paths (90,65). Other properties including the degree of fibrillation may be significantly different for the differing processing paths. Qualitative indications in the

literature are that the level of fibrillation can vary widely with draw ratio and draw temperature (74,65,111).

The effect of various conditions of drawing, annealing, and melt spinning on structure parameters as well as the relationship between structural and mechanical properties of polypropylene fibers have been considered extensively by researchers (99,65,111,52,64) in the Department of Chemical, Metallurgical, and Polymer Engineering at the University of Tennessee. The present study represents an extension of these researchers on fiber processing.

The purpose of this research project is twofold: first we seek to investigate the effects of spinning and drawing variables on the level of fibrillation produced during fiber formation. The second area involved an investigation of fibrillation by methods which are as quantitative as possible, especially quantitative small angle x-ray scattering (SAXS) procedures. The goal of these efforts is to find an innovative and useful method of quantitatively characterizing the degree of fibrillation.

CHAPTER II

BACKGROUND AND REVIEW OF LITERATURE

A. SURVEY OF PROCESSING

Generally, fibers can be spun from solutions of the polymer (wet and dry spinning) or from a polymer melt (melt spinning). Dry spinning is recommended for the use of continuous yarn filaments, polymers which can not be melted. It is used commercially for acrylic and cellulose, acetate fibers. Wet spinning is an important industrial process for polymers which cannot be melted and volatile solvents are unavailable. This process is used for rayon and acrylic fibers. The technical realization and physical mechanisms involved in dry spinning are more complex than those in melt spinning (74). High through put rates and lack of solvents make melt spinning the most convenient and efficient of the spinning procedures.

In the case of melt spinning, a fiber forming substance is melted for extrusion through a spinneret and hardened by cooling after it emerges. The cooling effect is sometimes increased through a perpendicular gas flow which is also designed to improve the stability of the spinning process. Fiber forming polymers must have chemically stable melts at technically available temperatures (60).

Melt spinning is usually followed by the drawing of solidified fibers leading to enhanced molecular orientation

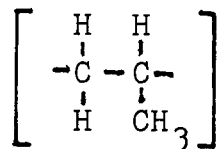
along the fiber axis and to improve the physical characteristics of fibers. Typical melt spun polymers are linear polycondensates (polyamides, polyesters) and crystalline polyolefine (polyethylene, polypropylene). A schematic diagram of melt spinning equipment is illustrated in Figure II.1(131).

B. THE STRUCTURE OF UNORIENTED POLYPROPYLENE

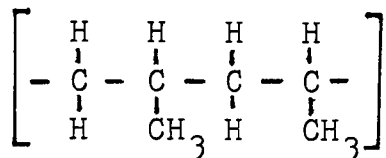
In this section the structural characteristics of polypropylene including specification of its molecular configuration and its various polymorphic forms will be considered. A complete description of structure variation with spinning and drawing conditions will be considered in later sections.

Molecular Configuration

The chemical repeat unit of polypropylene is



These units generally repeat in head to tail fashion as follows;



Polypropylene can be synthesized in a wide range of tacticities. These tactic forms are illustrated schematically

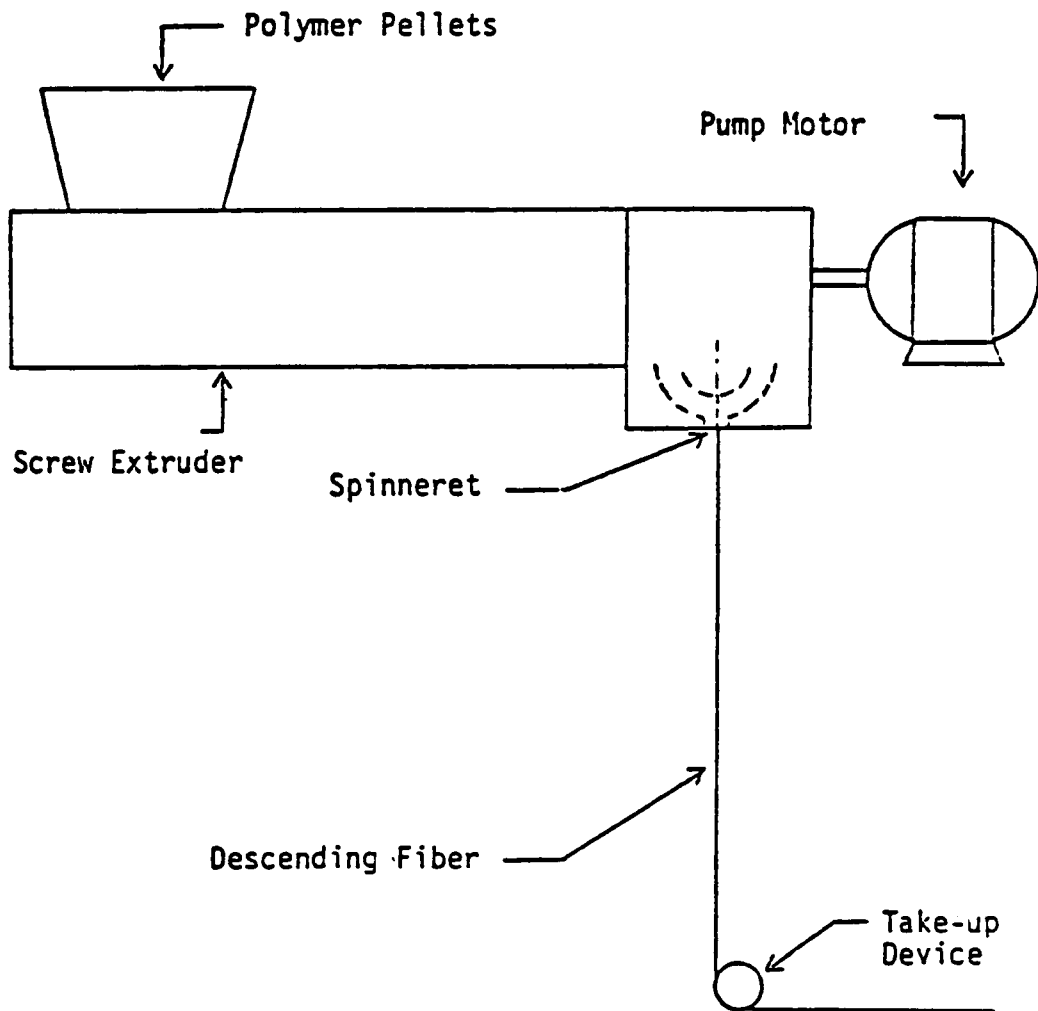


Figure II.1. Schematic diagram of melt spinning equipment.

in Figure II.2. The term "isotactic" identifies the particular spatial position of the propylene methyl group along the polypropylene carbon-chain backbone. In the isotactic case the methyl groups all fall on the same side of the main chain carbon back bone (Figure II.2a). This is in contrast to the syndiotactic case where each alternating methyl group is on the opposite side of the carbon backbone (Figure II.2b). Finally, random placement of the methyl groups along the main chain leads to atactic polypropylene (Figure II.2c).

The actual conformation of the polypropylene molecule is not a fully extended planar zigzag like that shown in Figure II.2, even in the crystalline forms. In its most common crystalline forms isotactic polypropylene has a 3_1 helix conformation as shown in Figure II.3. In this case it takes three monomer units to form the basic helix, the fourth monomer unit spatially repeating the 3_1 helix again. As a result of this conformation, the pendent methyl group, the C-H group, the main chain bond, and the CH_2 group all make an angle of about 72° approximately with the axis of the helix (Figure II.3).

When a melt of these helix chains is allowed to cool, some of the molecules will crystallize into folded-chain lamellae while others will not. In this way a two-phase system of non-crystalline and crystalline regions will be formed (90,3).

Isotactic and syndiotactic forms of polypropylene are

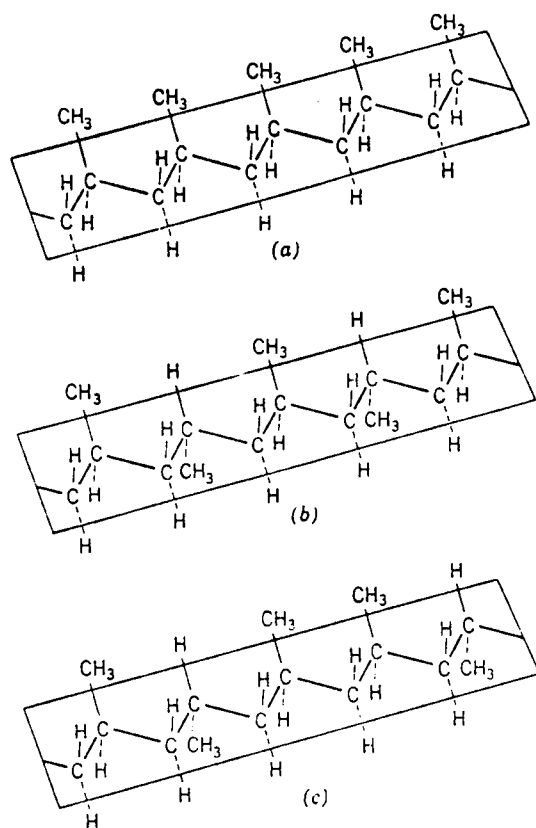


Figure II.2. Schematic representation of the spatial disposition of methyl groups in (a) isotactic, (b) syndiotactic, and (c) atactic polypropylene chain segments.

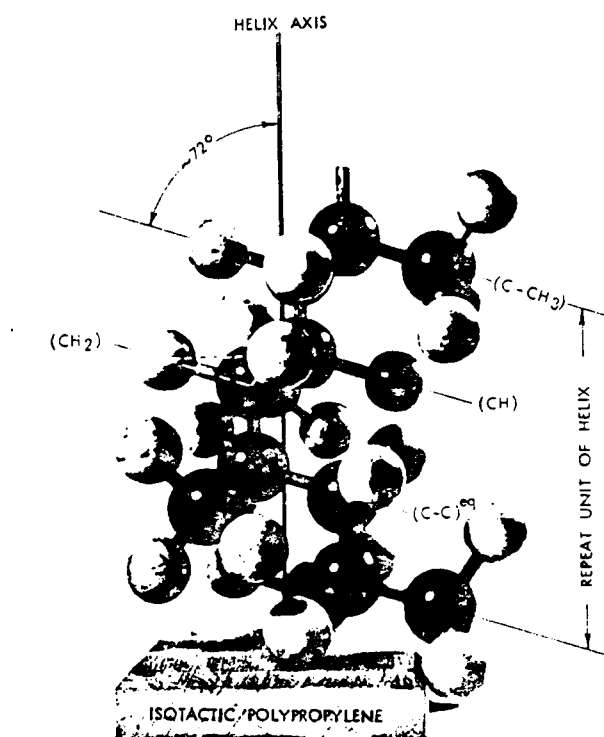


Figure.II.3. Conformation of isotactic polypropylene. The black balls represent carbon atoms; the gray balls represent hydrogen atoms.

partially crystalline, while the atactic form is necessarily amorphous, due to the lack of stereoregularity along the molecule. Commercial polypropylene are highly isotactic and have a high degree of crystallinity. These are of particular interest in this research.

Comparison of Crystalline Forms

There are three different crystalline forms (α , β , γ) and a so called paracrystalline form exist for isotactic polypropylene. The development of the various forms is dependent on the degree of isotacticity, molecular weight, thermal and mechanical history of the sample. The monoclinic or α -form is generally observed for both solution and melt crystallized samples which are prepared at atmospheric pressure (61). Natta and Corradini (70), and Turner, Jones et al (115) carried out studies of structure determination on the α -phase isotactic polypropylene. From wide angle x-ray (70), the identity period on the C-axis was found to be $6.5 \overset{\circ}{\text{Å}}$. From this it was concluded that the chains have a threefold helical configuration (3_1 helix), which corresponds to a regular alternation of trans and gauche bonds. The x-ray studies of Natta and Corradini (70) established monoclinic symmetry for the unit cell. The lattice constants are:

$$\begin{array}{ll} a = 6.65 \pm 0.5 \overset{\circ}{\text{Å}} & b = 20.96 \pm 0.15 \overset{\circ}{\text{Å}} \\ c = 6.50 \pm 0.64 \overset{\circ}{\text{Å}} & B = 99^\circ 20' \pm 1^\circ \end{array}$$

According to Natta and Corradini (70), the unit cell volume contains twelve monomeric units. The absence of hkl reflections with $h + k = 2n + 1$ confirms that the whole crystal lattice is C-centered. They reported that the most probable space groups for polypropylene is C_c . With such an assumption, the crystal structure of the α -form is shown in Figure II.4.

Rapidly quenching the polymer from the melt to below 130°C has been reported to result in a β -crystalline form (115). X-ray diffraction studies of Keith and Padden (47) suggest that the unit cell of β -form is hexagonal with constants $a = 12.71 \text{ \AA}$ and $c = 6.35 \text{ \AA}$. The β -phase is metastable in character and reverts to be a α -phase by recrystallization or deformation.

The γ form is only obtained by cooling the polymers from the melt. This γ modification occurs in small amounts, in specimens of unfractionated polypropylene which can be seen by the presence of a weak line at $4.42 \text{ \AA}$. It is characterized by five strong x-ray reflections, four of these reflections lie very close to the four of the five reflections of the α -form obtained by unoriented specimens. The γ -modification in specimens of low molecular weight have been observed by Addink and Bientems (4). They found a lesser crystalline form,

γ -modification in specimens of highly amorphous materials separated from the bulk isotactic material by extraction. However, isotactic polypropylene is capable of crystallizing in three polymorphic forms. The α -phase or monoclinic is

Source: G. Natta and P. Corradini, Nuovo Cimento, 15, 40 (1960).

the normal form in isotactic polypropylene.

Some investigators (30,40,43,91,123) have suggested that the structure might best be interpreted in terms of a two-component three phase model. The two components are crystallizable and non-crystallizable part of the bulk polymer and the three phases are crystalline, paracrystalline and amorphous. In this interpretation the paracrystalline phase is presumed to result from a highly disordered part of the crystallizable polymer and is distinct from the non-crystallizable part which is even more disordered. This interpretation is not universally accepted and other investigators have made different suggestions concerning the structure of the quenched polypropylene. Natta et al (69) termed the structure of a quenched polypropylene as "an unstable crystalline smectic modification". Their x-ray studies of the unoriented smectic form revealed two strong halos with d-spacing of $5.9 \overset{\circ}{\text{A}}$. Structural interpretations (40,123,69,6) suggest that smectic polypropylene has a short range three dimensional order with the molecular conformation the same as the crystalline α -form. A hexagonal crystal lattice for the smectic polypropylene has also been suggested by several investigators (30,111,103). The α -form converts to the smectic form by cold deformation (90,91,123) and the smectic form can be converted to the α -form (monoclinic) by heating (62).

Degree of Crystallinity

There are five principal methods used to determine the degree of crystallinity; 1) x-ray diffraction, 2) density measurements, 3) heat of fusion, 4) nuclear magnetic resonance, and 5) infrared absorption (3).

Generally, we assume that semicrystalline polymer to be a two phase system, crystalline and amorphous, where each has one set of properties in the range of samples of interest. Then the degree of crystallinity is given by,

$$x_c = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \quad (1)$$

where ρ_c and ρ_a are the crystalline and amorphous densities respectively and ρ is the density of partially crystalline "unknown" specimen. This formula can be applied to specific volume as follows;

$$\text{specific volume; } X_c = \frac{V_a - V}{V_a - V_c} \quad (2)$$

Crystallinity can also be determined from calorimetric measurement of,

$$\text{heat of fusion; } X_c = \frac{\Delta H_f \text{ Sample}}{\Delta H_f^* \text{ Pure crystalline}} \quad (3)$$

An x-ray differentiation method for determining x-ray crystallinity was given by Ruland (81). According to this method,

$$X_c = \frac{\int_{s_0}^{s_p} s^2 I_c(s) ds}{\int_{s_0}^{s_p} s^2 I(s) ds} K(s_0, s_p, D, f^2) \quad (4)$$

where $I_c(s)$ is the coherent intensity concentrated in the sharp Bragg peaks, f^2 is a mean square atomic scattering factor for polymer, D is the disorder function and s_0, s_p must be finite in practice. The degree of crystallinity for spun fibers has been found to be about 50-60 percent by several investigators (37,90,65,123).

C. TECHNIQUES FOR CHARACTERIZATION OF ORIENTED POLYMER

Crystalline Orientation

A quantitative expression for the average orientation of polymer chains in uniaxially oriented samples was originated by P.H. Hermans and co-workers (38). Such a factor takes the form;

$$f_c = \frac{1}{2} (3 \overline{\cos^2 \theta_{c,z}} - 1) = 1 - \frac{3}{2} \overline{\sin^2 \theta_{c,z}} \quad (5)$$

where $\overline{\cos^2 \theta_{c,z}}$ and $\overline{\sin^2 \theta_{c,z}}$ represent respectively the mean square cosine and sin (averaged over all the molecular) of the angle between the fiber axis and the c-crystallographic axis.

Stein (109) generalized equation (6) for the three

crystallographic axes to specify the degree of orientation with respect to reference direction.

$$f_a = \frac{1}{2} (3 \overline{\cos^2 \theta_{a,z}} - 1) \quad (6)$$

$$f_b = \frac{1}{2} (3 \overline{\cos^2 \theta_{b,z}} - 1) \quad (7)$$

$$f_c = \frac{1}{2} (3 \overline{\cos^2 \theta_{c,z}} - 1) \quad (8)$$

The c-axis usually refers to the polymer chain axis and equation (8) to the Hermans orientation factor. The corresponding geometry is shown in Figure II.5. From the above observation the range of the value for $\cos^2 \theta$ and f for three states of orientation is shown in Table I.

TABLE I. ORIENTATION WITH RESPECT TO REFERENCE DIRECTION Z.

PARAMETER	PARALLEL	RANDOM	PERPENDICULAR
$\cos^2 \theta$	1	1/3	0
f	1	0	$-\frac{1}{2}$

When the crystallographic axes are orthogonal;

$$\cos^2 \theta_{a,z} + \cos^2 \theta_{b,z} + \cos^2 \theta_{c,z} = 1 \quad (9)$$

$$\text{from which it follows that, } f_a + f_b + f_c = 0 \quad (10)$$

The three orientation functions are not independent with only two of them are required to characterize the orientation. The orthogonality relationship in this case demands that c, a b crystal axes are perpendicular.

Determination of the f_j generally involved WAXS measurements. In polyethylene f_a and f_b may be readily

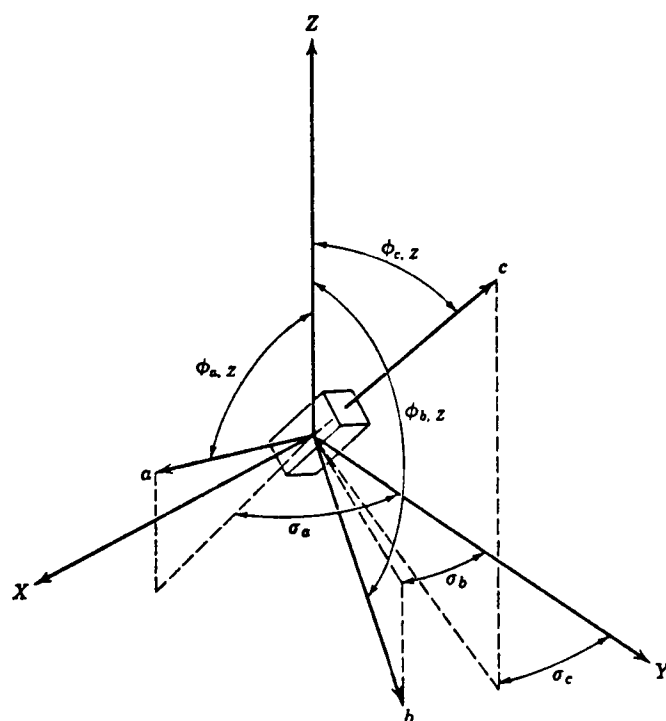


Figure II.5. Stein's coordinate system for specifying orientation modes in orthorhombic polymers.

obtained directly from (200) and (020) wide angle x-ray (WAXS) reflections and f_c from equation (10).

Problems exist in determining the f_j for the monoclinic isotactic polypropylene. In monoclinic polypropylene there is no set for reflecting planes which are perpendicular to the c-axis. Further a, b, and c axes are not mutually orthogonal the relation between f_a , f_b and f_c in equation 10 does not hold. Wilchinsky (120) derived equations relating the variation of intensity with azimuthal angle of (040), (110), (130) reflections in polypropylene to the orientation function parameter which characterize the b and c axes.

$$\overline{\cos^2 \theta} = 1 - \frac{(1 - 2 \sin^2 \rho_2) (\overline{\cos^2 \theta_1}) - (1 - 2 \sin^2 \rho_1) (\overline{\cos^2 \theta_2})}{\sin^2 \rho_1 - \sin^2 \rho_2} \quad (11)$$

Where ρ is the angle between the b axis which can be calculated from cell dimensions and the plane normally by the subscripts refer to the respective planes. θ is the angle between c-axis and reference direction.

Fiber Birefringence

Fiber birefringence is defined as the difference in the principal refractive index parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the stretch direction for a uniaxially oriented specimen.

$$\Delta n = n_{\parallel} - n_{\perp}$$

The refractive index, is a measure of the light velocity

in the medium and is related to the polarizability of the chains. The final measured birefringence is a function of contributions from the polarizabilities of all the molecular units in the specimen.

The light velocity in the amorphous phase will be varied from that in the crystalline phase. There is a difference in the principal polarizability parallel, $p_{\parallel}$, and perpendicular, $p_{\perp}$, to the chain axis within each phase, since the molecules are also optically anisotropic. If all the anisotropic molecules in a phase are randomly distributed the average contribution of this phase to the refractive index of the sample will be the same in all directions and the contribution to the birefringence associated to the phase, $\Delta_i = n_{\parallel i} - n_{\perp i}$ will be zero.

In addition, if the sample is an unoriented two-phase mixture consisting of crystalline and amorphous materials, the total birefringence will still be zero. In this case all anisotropic molecules, regardless of phase, are randomly oriented in the sample and the average contribution to the refractive index will also be the same in all directions.

If all the molecules of the two phase model are perfectly aligned parallel to the stretch direction, the birefringence will be a combination of the intrinsic birefringences of the individual phases Δ_c^0 , Δ_{am}^0 , weighted according to the volume fraction of each phase.

The measured birefringence of a partially oriented

sample will also depend on the orientation factors (f_c, f_{am}). For a uniaxially oriented, polycrystalline polymer, the total birefringence, Δn is related to both the crystalline and amorphous birefringence through,

$$\Delta n = \bar{X} \Delta_{cry}^0 f_c + (1 - \bar{X}) \Delta_{amorph}^0 f_{amorph} + \Delta_{form} \quad (12)$$

where f_{amorph} and f_{cry} are the amorphous and crystalline orientation functions, $\bar{X}$ is crystallinity, Δ_{cry}^0 and Δ_{amorph}^0 are intrinsic birefringence of perfect oriented crystalline and amorphous material. If the Δ_{cry}^0 , Δ_{amorph}^0 , $\bar{X}$ and f_c (from WAXS) are known, birefringence may be used to estimate f_{amorph} , Δ_{form} is usually considered small.

Amorphous Orientation

The crystalline orientation functions discussed earlier relate to the crystal regions in the polymer. The Hermans orientation function can also be used to quantitatively describe the level of orientation in the amorphous regions. However, this quantity is not easily obtained from x-ray diffraction measurements. To estimate the amorphous orientation it is usually common to use a physical property which is depend on the orientation in the specimen. For partially crystalline sample, the measurement of the smorphous orientation function is obtained using an expression similar to equation (12). In this case the crystalline contribution

is obtained by methods described previously, and the difference between the crystalline contribution and the average property gives an amorphous contribution which one can easily obtain the amorphous orientation function (f_{am}).

Samuels (90) has shown that the use of Hermans equation (12) to determine f_{am} requires knowledge of the values, such as, birefringence, crystalline orientation function, f_c , Δ_c^0 and Δ_{am}^0 and crystalline fraction ($\bar{X}$).

Morphology and Superstructure

The morphology and superstructure of polypropylene can be examined by various methods. X-ray scattering and electron microscopy are the most powerful methods for investigation of the crystal morphology of fibers. The small angle x-ray scattering is useful in determining the morphology of domains from 20 Å up to more than thousands of angstrom units. Crystallites (20-500 Å), amorphous periodicities (20-2000 Å), chain folding periodicities (50-300 Å), and voids (20-10,000 Å) can be studied by this technique (3,60,72,103,104,74). The size of the structural domain is related to the scattering angle by the Bragg's law relationship;

$$n\lambda = 2d \sin \theta \quad (12)$$

where θ is the angle that radiation makes with the diffracting plane (3). Frequently the only cooperative reflections that appear in the SAXS pattern occur as a result of periodic

arrangement of crystal lamellae and intercrystalline disordered regions. Measurement of the reference point of the interference maximum makes available direct calculation of the so called long period (90). The generally accepted morphology of uniaxially oriented filaments and films was proposed by Keller and Machin (48) based on fundamental studies of SAXS and electron microscopy.

Optical methods such as birefringence, light scattering, and microscopy yield information on fiber superstructure (123). Scanning electron microscopy is a most useful method of studying fiber superstructure (52,111).

Small Angle X-ray Scattering

An inhomogeneous system may consist of either diffuse or discrete effects. Guinier (32) showed that a single particle of colloidal dimensions can produce a characteristic diffuse small angle scattering pattern and that many identical particles at sufficiently large and irregular distances from each other will produce a total scattering that is simply the sum of the scattering of the individual particles. It is of prime importance to realize that a diffuse small angle scattering pattern is never subject to an unequivocal structural interpretation on the basis of the x-ray data taken alone. Specimens which show identical scattering curves may be designated scattering equivalent systems (78).

In principle the following types of ambiguity must be considered in the interpretation of diffuse small angle scattering; a) it is not possible to distinguish the scattering by a system of particles in space from the scattering by a complementary system of micropores in a solid continuum, b) it is not possible to differentiate without some degree of uncertainty the effects due to particle shape from those due to polydispersity. It is often difficult to determine to what extent the scattering curve is determined by the isolated particles and to what extent by the interparticle interferences (3).

Evidence now shows that the best interpretation of diffuse scattering from solid polymers is in terms of microvoids or intermediate space. Much detailed theory was presented by Porod (78,79) to show that when the matter is dense enough to cause interparticle interference, the reciprocity rule dictates that the rest of the scattering curve is caused by the interstices or voids. Statton (102) proposed that voids must be considered the cause of the scattering; this was later quantitatively confirmed by Hermans, Heikens and Weidinger (38). In 1962, a review of diffuse small angle scattering by Statton (103) extended to all polymers the interpretation that the most probable cause of the scattering is voids. In a variety of ways it was shown that the inhomogeneity of electron density is microvoids. He reported that the microvoids are small regions in

the polymer which are usually less than 100 Å. In particular Statton (104,103) makes the following points, 1) it is normal to find intense diffuse scatter in the small angle patterns of synthetic as well as natural fibers, and very weak scattering is the exception rather than the rule, 2) a fiber treatment that produces a decrease in the diffuse scatter is accompanied by an increase in density, 3) the degree of crystallinity is unrelated to the diffuse scatter as is shown by large variations in the amount of diffuse scatter with no change in the crystalline fraction and, conversely, by observation of large changes in the crystalline fraction with no appreciable change in the intensity of the diffuse scatter, 4) most commercial fibers show a level of diffuse scatter, 5) microvoids are a logical consequence of the fact that long chain polymers cannot efficiently fill all space. Thus the voids maybe unfilled spaces around polymer chains, around fibrils, or between lamellae.

The amount of diffuse x-ray scattering given by a fiber depends profoundly upon the method used to form the fiber. Large void contents are promoted by those fiber spinning procedures that result in rapid precipitation of the fibers from solution for example, wet, dry and dispersion spinning. Such a high level can be subsequently reduced by the annealing effects of thermal after treatments. Relatively small numbers of microvoids are produced by solidification of a

viscous polymer from its melt, by slow exaporation of a polymer solution, or by spinning procedures that permit slower precipitation from solution (3).

Extension of melt spun fibers by drawing processes has the effect of increasing the equatorial dimension of the scattering at the expense of the meridional dimension, thus signifying an elongation of the voids parallel to the direction of stretch. In general, the amount of void elongation increases as windup tension is increased (3,103,104).

If discrete interferences appear in the small angle x-ray scattering patterns of oriented polymers, they are usually observed in only one direction, most commonly on the meridian. The meridional reflections denote some degree of large-scale periodic character in the structure parallel to the fiber axis. In terms of the "fringed micelle" model the long period spacing obtained from the first order meridional reflection can be most usefully interpreted as the mean distance between the center of successive crystalline regions along the fiber axis (38,103). This initial interpretation seems also valid for the newer concept of chain folding within the crystalline regions (106).

An important feature of the long period meridional spacings of polymer fibers is the dependence on the crystallization and annealing temperatures. Many significant studies of this long spacing phenomenon have been made (124,59) with the final long period spacing depending on both the time and

temperature of annealing. Figure II.6 shows the dependence of the long period spacing of polyethylene crystals on the annealing temperature as determined by Statton and Geil (108) and Fischer (28). A possible mechanism permitting the increase in long period and the extension of the fold period by means of migration of point defects along the molecular chain under annealing conditions has been suggested by Reneker (79) and is shown schematically in Figure II.7.

D. STRUCTURE VARIATION WITH MELT SPINNING CONDITIONS

The original study of spinning conditions on fiber structure was carried out by Carothers and Hill (15), Keller (49,50), Ziabicki and Kedzierska (125,128,129) in the late 1950's and early 1960's further investigated the crystallization and orientation of melt spun fibers.

On-line studies of structure development during melt spinning have been reported for polyethylene (HDPE) by Katayama, Amano and Nakamura (45) and by Dees and Spruiell (24), using wide angle x-ray diffraction. Polypropylene (PP) has been investigated in similar experiments by Katayama et al (46), Nadella, Henson, Spruiell and White (37,99,100), Shimizu and Shimazaki (94) and by Ishizuka and Koyama (42). The rate of crystallization was observed and found to increase rapidly with applied stress. Increasing draw down was found to first orient the 'b' axis perpendicular to the

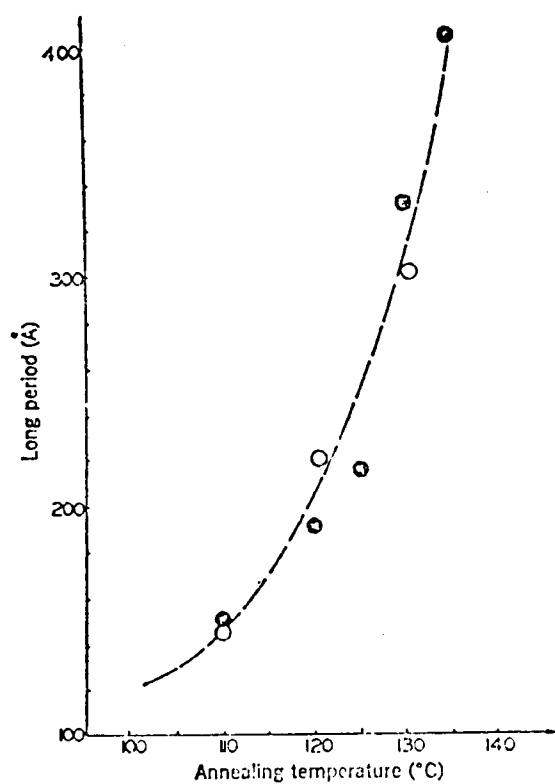


Figure.II.6. Dependence of the long period of polyethylene crystals on the annealing temperature. Closed circles-measured at room temperature by Statton and Geil (108). Open circles measured at annealing temperature by Fischer (28).

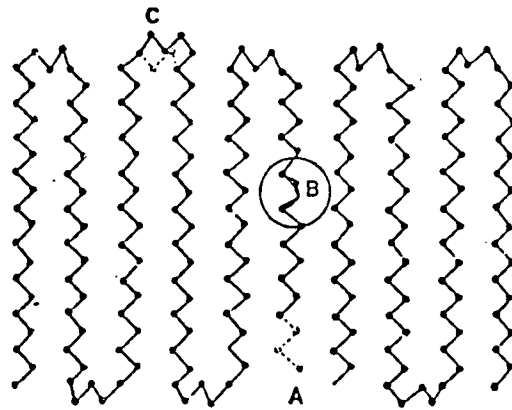


Figure II.7. Illustration of point defects originating at A, progressing through the lattice at B, and extending the fold period at C. (Reneker, 79).

fiber axis, "c" axis orientation increases more slowly. The same tendency to "a" axis orientation is observed at low draw down in Low Density Polyethylene(LDPE) and High Density Polyethylene (HDPE). At high draw down "c" axis orientation domainates and the "a" axis becomes perpendicular to the fiber axis. Polypropylene shows a lesser tendency to this type of "a" axis orientation. A striking development of bimodal orientation is however observed in this polymer. Some investigators (24,64,99,100) have interpreted these structural changes in terms of Hermans-Stein orientation factors. Nadella et al (45) have shown that the orientation factors in polypropylene depend upon the spinning stress levels rather than kinematic variables.

Katayoma et al (46), Nadella et al (65) and Shimizu and Shimazaki (94) in their studies of on-line birefringence in polypropylene melt spinning found that after a first gradual ascent of birefringence, it increases abruptly and then levels. The first gradual and second abrupt ascents are attributable to the deformation of filaments and the crystallization respectively. It was found that the birefringence of the molten polymer filament is proportional to the spinning stress.

Oda, et al (71) have studied the birefringence of vitrified polystyrene. They concluded that the negative values of the birefringence have qualitative significance. It shows that the birefringence has originated in the molten

state where the stress coefficient for polystyrene is negative and was frozen in.

Sheehan and Cole (91) were the first to investigate the development of crystalline structure in polypropylene. They observed x-ray patterns of undrawn polypropylene filaments which are spun with different molecular weight under various conditions of extrusion and quenching temperature. The x-ray patterns after being cooled by quenching into water show smectic form of polypropylene. Those fibers which were spun into air were the monoclinic form.

Kitao, et al (52), Samuels (90) and Nadella et al (64) evaluated the contributions by the amorphous chains to the total orientation in melt spun polypropylene fibers. They showed that the orientation developed in the crystalline regions during melt spinning is much larger compared to the orientation in the amorphous chains. Samuels (90) also explained the structure of oriented melt spun polypropylene fibers. H_v Small Angle Light Scattering (SALS) show that the spun fibers were made up of 0.7μ spherulites which their long axes were normal to the fiber axis direction. The spun fiber was assumed to be composed of inhomogenously deformed interspherulitic fibrillar links and spherulites.

Dees and Spruiell (24) proposed a detailed morphological model for melt spun linear polyethylene based on the experimental studies and suggestion of Keller and Machine (48). This work and the other extensive experimental studies of

structure development during melt spinning of polyethylene (1,23,118), polypropylene (57) and polyoxymethylene (51) fibers were reviewed by Spruiell and White (50). They concluded that the development of morphology in polyethylene, polypropylene, and polyoxymethylene occurs with increasing take-up velocity and stress shows numerous similarities. Nadella, Henson, Spruiell and White (64) concluded that spinning variables such as polymer molecular weight, take-up velocity, flow rate, melt temperature, all effect the morphology of the spun fibers, but the combination of these effects on morphology can be inferred from their effect on spinline stress.

Melt spun polypropylene exhibits bimodal orientation as mentioned previously, Clark (18), and Clark and Spruiell (19) proposed morphological models for crystallized polypropylene. Their interpretation of bimodal orientation consists of a row structure of planar lamellae interconnected by tie molecules, which give rise to the c-axis oriented contribution.

Another aspect of polypropylene are the hard elastic fibers and films. Clark (18) and Sprague (98) have proposed detailed models of morphology for highly crystalline polymers which under stress produce "hard" elastic fibers and films. These models have considered these hard elastic fibers and films to have a developed "row structure" morphology. Evidence for this structure includes SAXS and Transition Electron Microscopy (TEM).

E. DRAWING AND STRUCTURAL CHANGES DURING DRAWING

Often, spun fibers are not highly oriented, anisotropic nor have high mechanical strength. Drawing such fibers results in a reorganization of the substructure which transforms this structure of low anisotropy into a highly anisotropic and highly oriented fiber structure with high tensile strength and elastic modulus (90).

During the melt spinning process of fibers such as polypropylene, crystallization including some orientation develops, while the majority of orientation occurs during drawing.

Observation of Necking

Generally polymeric fibers form necks and shoulders during cold drawing. In 1932 Carothers and Hill (14) observed phenomena, during the transformation of unoriented molecular structure of oriented molecular structure of fiber. Fankuchen and Mark (31) analyzed the necked zone on cold drawn nylon-66. They described orientation in unnecked and necked regions from microbeam x-ray diffractions, Kasai and Kakudo (44) investigated the continuous structure change in the necking zone of the cold drawn polyethylene. They also proposed a series of suitable models for continuous structure change in necking. White, Dharod and Clark (118,25) investigated

the drawing operation of high and low density polyethylene. In cold drawing of HDPE they observed necking with a higher degree of crystallinity and orientation in the necked zone. Also, they found in the necked and unnecked regions the crystalline orientation factor unchanged with increasing total draw ratio. Sze, Spruiell and White (111), Nadella, Spruiell and White (65), Kitao et al (52) observed development of necks and shoulders during cold drawing of fibers. They stated that the polymer in the neck is a very different material with considerably higher modulus than in the unnecked modulus than in the regions which gradually disappear as the filament is extended. Also the fibers which have a higher spin orientation show reduction in the necking elongation.

Changes in Crystalline Structure

Sobue and Tabata (95) and Wyckoff (123) observed the transformation of monoclinic crystalline structure of polypropylene into the paracrystalline structure by the cold drawing. On drawing completely oriented isotactic polypropylene fibers in water 70°C, Sobue and Tabata (95) noted that the crystalline structure is transformed to the paracrystalline structure. Wyckoff (123) found the complete conversion of the crystalline structure to the paracrystalline state at a cold draw ratio of seven. Annealing of highly drawn polypropylene films did not change the orientation of crystallite under various annealing conditions, but isometric

annealing showed improvement in samples with low orientation of the crystallites. The transformation of paracrystalline state (smectic) to crystalline state started at 70°C, reached the halfway point at 100°C and was complete at 145°C.

Nadella et al (65), Kitao, Spruiell and White (52) have presented more recent studies of drawing polypropylene fibers. The WAXS patterns of the cold drawn samples show a high degree of broadening which may be considered to result from a decrease of crystallite size and enhanced lattice strains and defects. This broadening increases with draw ratio. A possible interpretation of these results is that transformation of monoclinic state of as spun filaments into a paracrystalline state by cold drawing. This structure may be similar to the "smectic" produced by rapid quenching from the melt (95,123). Nadella et al (65), also concluded that the hot drawn fibers usually yielded somewhat more perfect (and larger) crystalline domains than the cold drawn drawn and annealed fibers.

A decrease in the density of polyethylene during cold drawing was observed by Bettelheim and Stein (11), White et al (118). Also densities of hot drawn, cold drawn and annealed fibers are slightly higher than those of the melt spun filaments indicating small increases in crystallinity.

Changes in Orientation and Morphology

Stein (109) studied uniaxial orientation in stretched polyethylene by x-ray diffraction, birefringence and infrared dichroism. He noted that crystallite orientation is higher than that of the amorphous orientation.

Sheehan and Cole (91) studied drawing operation on polypropylene filaments followed by annealing at 100°C. They found that filaments with "smectic structure" orient more rapidly than the "monoclinic crystal structure" filaments and can be drawn more easily. But with the draw ratio above 25 the crystals were completely oriented regardless of any crystalline structure. Studies on polypropylene by Samuels (86) show that cold drawn fibers which were annealed very close to the crystal melting temperature have yielded biaxial orientation. Nadella et al (65) noted that hot drawn fibers often show a better molecular orientation than cold drawn and annealed fibers.

Samuels (85) studied the morphological changes of fiber structure during drawing of spun fiber at 90°C and compared them with the same fiber after heat setting of 140°C. He found that morphological transformations were contrasting in maximum and minimum range of extension. In the low draw region the greater deformation occurs in the polar region of spherulites. During further drawing, the non-crystalline region orients and he suggests the highly oriented

crystals resist cleavage or further orientation. At high temperature (135°C) the lamellae are larger and more perfect and thus less deformable. In the high draw region, the spherulitic structure transforms into a microfibrillar structure.

Voiding and Fibrillation

The formation of microvoids in polypropylene films during stretching was observed by Wyckoff (123). His SAXS patterns indicated that the visual whiteness produced during cold drawing was related to lamellar voids elongated in the draw direction.

Peterlin (72,73,74) has made an intensive study of the structural metamorphosis that occurs during the deformation and annealing of polymers. Figure 8 illustrates schematically Peterlin's ideas for fiber formation by mechanisms of chain tilting, slip, and breaking off of blocks of folded chains with subsequent re-formation of folded-chain domains constituting a fiber of different orientation. He reported (74) that the fibrillation often observed is a consequence of longitudinal voids which results from extreme fluctuation of deformation during the transformation of the original more or less spherulitic sample into the final fiber structure. Depending on lamellar orientation and stacking ie., on the morphological properties of the starting material, the plastic deformation during drawing varies locally between

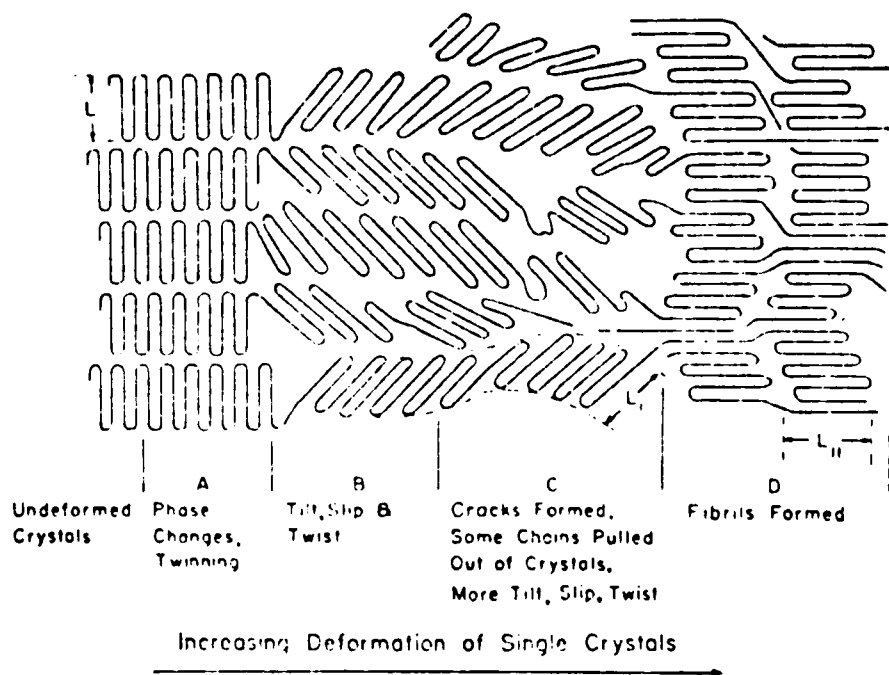


Figure II.8. "Mechanisms of chain tilting"
Peterlin's model.

rather wide limits. Each fibril contains material resulting from one stack of lamella and hence has a nearly constant draw ratio. The boundary between adjacent fibrils is more discontinuous with increasing draw ratio and eventually becomes a long cylindrical void completely separating the fibrils.

Samuels (90) studied quantitative characterization of deformation in polypropylene fibers. He observed microvoids in the drawn fibers by using dark field microscopy. This suggests that deformation in polypropylene fibers is accompanied by void formation. Fibers drawn at 90°C and heat set at 140°C formed microvoids which oriented transversely at low extensions and longitudinally at high extensions. Sakaoku and Peterlin (82) carried out drawing of this polypropylene films. Microfibrils with lateral dimensions of 200 Å at small draw ratio, originating in micronecks of the original crystal lamellae, were obtained in isolated zones exhibiting maximum local strain separated by large regions of much less deformed material. The inhomogeneity of adjacent bundles of microfibrils create a great many longitudinal voids with less or more disoriented microfibrils bridging the gap.

Samuels (90,86,87) on cold drawing polypropylene observed fibrillation during cold drawing of the fibers. Muzzy and Hansen (63) investigated fibrous structure formation in cold drawing of polypropylene. Their optical photomicrographs of samples drawn at 60°C indicated at the

draw ratio of 6.0, the disruptions are highly oriented and have the appearance of micronecks running parallel to the draw axis. The persistence of the spherulites as integral units up to a draw ratio of at least 10, was clearly shown. Electron micrographs of fracture surfaces at this draw ratio are dominated by a still finer scale fibrous structure. At a draw ratio of 20, the fibrous structure is more completely developed.

Sze, Spruiell and White (111) carried out extensive study of the influence of drawing, twisting, heat setting and untwisting on the structure and mechanical properties of melt spun high density polyethylene. Their SEM photomicrographs clearly exhibit that the drawn fibers have a fibrillar superstructure. SAXS patterns show a major reduction of the intensity of the meridional scattering compared to the melt spun fibers and very intense diffuse equatorial scattering. They concluded that degree of fibrillation clearly increases with increase in the draw ratios beyond the natural draw ratio.

Nadella, Spruiell and White (65) investigated the influence of cold drawing (25°C), hot drawing (140°) and annealing (140°) on the structural and mechanical properties of various melt spun polypropylene filaments. They concluded that hot drawing is viewed as causing less fibrillation than cold drawing. The samples with low as-spun orientation exhibit greater fibrillation than those with high as-spun orientation.

Kitao et al (52) studied influence of drawing and twisting of polypropylene filament. The general view of the mechanisms of drawing which they formed from their study is similar to that of Peterlin (72), Sze, Spruiell and White (111).

F. MECHANICAL PROPERTIES OF THE SPUN AND DRAWN FIBERS

Melt Spun Fibers

Since the work of Carothers and Hill (15) the mechanical properties of synthetic fibers have been extensively studied. Most of the early work was primarily concerned with the properties of drawn fibers rather than as spun filaments.

Carothers and Hill (15) in the early studies of fiber formation noted that fiber strength increases with an increase in draw down tension. Krassig and Kitcherene (74) reported that tensile strength in rayon increased linearly with the square of Hermans orientation factor.

Effects of melt spinning variables on the mechanical properties of high density polyethylene fibers were studied by Higgins and Bryant (127). They reported that the tenacity and stiffness modulus of melt spun polyethylene fiber are functions of the logarithm of take-up speed.

Ziabicki (127) concluded that in undrawn polyester and polyamide fibers an increase in birefringence lead to an increase in tensile strength and a decrease in elongation to break.

The mechanical properties of melt spun polyethylene fibers have been extensively studied by Abbott and White (1), Dees and Spruiell (24), and White et al (118), Abbott and White (1), Dees and Spruiell reported that the mechanical properties of the spun polyethylene fibers depend primarily upon the orientation rather than crystallinity level. Their studies indicate that as the crystalline c-axis orientation function, f_c , increases the tensile strength and modulus also increase, but elongation to break decrease.

Henson (37), Spruiell and White (99) and Nadella et al (65) studied the mechanical properties of melt spun polypropylene fibers. They noted that the filaments spun at higher stress have higher modulus, tenacity strength and lower elongation to break. The variation of the modulus, tensile strength and elongation to break with the c-axis crystalline orientation function (f_c) was found to be similar to polyethylene. The true stress at fracture decreases with f_c . Spruiell and White (99) based on this result, suggest that higher tensile strengths can be obtained in drawn fibers which have low orientation as melt spun with spherulitic structure and then drawn to very high draw ratio.

Nadella et al (65) reported that the tensile properties of the spun polypropylene fibers correlated with the spinline stress. It was concluded that this was a result of the fact that the morphologies of the filaments were controlled by the spinline stress.

Drawn Fibers

Drawing of the melt spun fibers considerably increases the Young's tangent modulus and tensile strength of the fibers while decreasing the elongation break. This is implicit in the work of Carothers and Hill (14) and other early investigators (49,91,111,118,122).

A study of properties and structure of iostactic polypropylene was carried out by Sheehan and Cole (89). They concluded that; 1) the higher oriented filaments as spun, the lower the tenacity of the drawn fibers, 2) modulus increases and elongation to break decreases with increasing draw ratio and tenacity, and 3) draw ratio increases tenacity irregardless of molecular weight.

Samuels (80) concluded that yield stress increases with increasing molecular orientation, while decreasing with temperature and increasing rate. This correlated directly with average molecular orientation. Average molecular orientation can be defined as,

$$f_{av} = x f_c + (1-x) f_{am} \quad (13)$$

For spherulitic samples, by increasing the orientation a yield strain increases. Samuels (87) also reported a lower tensile modulus in polypropylene fibers drawn at 90°C (below the crystal mobility temperature) compared with fiber spun after drawing at 90°C with subsequent heat setting under tension at 140°C (above the crystal-mobility temperature).

He found that the drawn fibers which are less crystalline and less oriented obtain a low tensile modulus compared to the heat set fibers. He observed a break in the linearity in the tensile modulus draw ratio curves in the draw range of 2-2.5X and from morphological examination concluded that void formation and conversion of spherulitic to the microfibrillar structure was the primary contributor to the observed modulus behavior.

White, Dharod, and Clark (118), Sze et al (111) in their study of the drawing of polyethylene fibers observed an increase in Young's modulus and tensile strength and a decrease in elongation to break with increasing molecular weight. Nadella et al (65) showed that the mechanical properties of the spun, hot drawn or cold drawn and annealed fibers could all be correlated with birefringence measurements.

Kitao et al (52) investigated structural and mechanical property variations in melt spun polypropylene filaments, induced by drawing, twisting, annealing and untwisting. They concluded that the tensile strength and elastic modulus of the cold drawn and hot drawn fibers similarly increased while the elongation to break decreased, at a given draw ratio.

In heat-setting of cold drawn samples, the elastic modulus decreases and this decrease is greater at high draw ratios. The tensile strength is not affected by annealing as much as the modulus. However, cold drawn samples show no

appreciable decrease of tensile strength on annealing at 140°C while there is a considerable increase in the density.

G. PILLING IN PERFORMANCE OF TEXTILE FIBERS

An area of textile performance which may be related to fibrillation is pilling. Pilling has been recognized as a problem in performance of textile fabrics. This problem usually is associated with fabrics made from staple fiber yarns, the effect has become more acute with the development of synthetic fibers. It proceeds through three stages; a) fibers are surfaced as a result of some mechanical action on the fabric, 2) surfaced fibers entangle or mat into the familiar configuration of a pill and 3) the pills wear off or are pulled away from the fabric. Pills are usually formed as balls but sometimes appear as ridges.

Baird, Hatfield and Norris (8) carried out studies of pilling of nylon, and nylon blended fabrics. They used a laboratory apparatus to investigate the factors affecting pilling. The following variables were studied; nylon content, fiber denier and staple length, yarn twist, doubling yarns, ends and picks types of weave, milling, heat setting, dyeing, wetting and flexing. The effect of cropping and of applying certain chemical finishes, the forces which required to remove pills from fabrics were also considered. They concluded that pilling is caused by protruding fibers which entangle when a fabric is rubbed. The magnitude of pilling depends

upon the number and length of protruding and the ease with which they can bend round one another. When the fibers are weak the fabric shows little or no pilling, because pills break off easily. They also reported that pilling is reduced by increasing yarn twist, using doubled yarns instead of equivalent single yarns, increasing picks and ends appreciable, and cropping of the fabric. Chemical treatment such as methoxy-methylated nylon (calaton CA) in 80/20 ethyl alcohol/water solution, aqueous dispersions of polyvinyl acetate with and without plasticiser, polyvinyl butyral (merion BR) and a modified acrylic (dicrylan WG) were applied to a 100 percent nylon fabric and also to commercial nylon blended fabrics. They concluded that Calaton CA gives the most effective reduction in pilling but Merlon BR, Dicrlan WG and polyvinyl acetate all give similar reduction in pilling.

The effect of heat setting nylon yarn and fabric were concerned where 100 percent nylon staple fabrics were heat-set for a day over a range of temperature and pressures also under 25 lb/sq. inch steam pressure. These treated fabrics pilled slightly more than the untreated fabrics. The mechanism of pilling was studied by Dennison (24), Daniel and Mead (31), Conti and Tassinari (22), Trhimm (113), Brand and Bohmbalk (12) and many others. Daniel et al (31) investigated the mechanism of pilling by using an instrument for time lapse picture studies. Motion pictures of fabric subjected to an abrading action showed that the abradant acted on

exposed fiber sections to pull loops which then opened to form fuzz. A pill formed quickly when the fuzz density reached a critical level. The fibers were then twisted and entangled, gradually involving nearby fibers. As the abrading action continued, pills wore away. He also used various techniques to measure fuzz tendencies of different fibers. He found that nylon is most prone toward fuzzing due to high strength, a moderate interfiber friction, and low stiffness. Wool and acetate are low tenacity fibers, so the fibers break instead of pilling out, resulting in short fuzz. Rayon, "polyester" and "polyacrylnitrate" are intermediate in behavior. "Polyester" has a high strength but also a high interfiber friction and stiffness. Rayon has a moderate strength, a high stiffness, and a low interfiber friction. "Polyacrylnitrate" has an intermediate strength, a high interfiber friction, and a high stiffness. Flex life and abrasion resistance appear to exert a relatively unimportant contribution until later stage of the abrading action.

Based on studies of pill formation, Gintis and Mead (31) observed that the amount of fuzz tends to rise sharply with the brushing time but to level off in a time much shorter than that of pill formation and wear-off.

The numerical distribution of fibers in pills was studied by Conti et al (22). They examined two fabrics, Sample A was a plain jersey fabric having a weight of about 170 g/m^2 . It was knitted from a yarn of 29 tex and twist

factor 85, made from standard polyethylene terephthalate staple fiber with a trilobal crosssection. It was knitted from a yarn of 29 tex and twist factor 100, made from modified medium antipilling polyethylene terephthalate staple fiber with a round-cross section. For this examination the "Atlas random pilling tested" was used. They proposed a model which shows that the entanglement pilling mechanism can be considered a random phenomenon with a probability constant.

Brand and Bohmfalk (12) proposed a mathematical model of pilling. They considered the fabric as an infinite source of fuzz. A simplified model for the mechanism of pilling proposed by Conti and Tassinari (22). This model is characterized by three parameters W_0 (the number of pills), d (the rate of pill formation), and W (the pill-wear off rate) to define the shape of the curve of the total number of pills on a sample during normal wearing off.

CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURES

A. GENERAL CHARACTERIZATIONS OF POLYPROPYLENE RESINS

In the present research three different commercially available polypropylenes of high tacticity and varying molecular weights were studied to determine the effect of molecular weight properties, melt spinning and drawing variables on the level of fibrillation of polypropylene fibers. Two of the resins were from Hercules Inc. (Profax 6423, Profax 6323) and the other an experimental polymer supplied by Diamond Shamrock Inc. (5831-106-7)

The specific viscosities of Decalin solutions of polypropylene were determined with a cannon-Ubbelohde viscometer at 137°C as described by Nadella (65). Reduced viscosities could be plotted against concentration using the Higgins empirical equation to determine the specific viscosity, η_{sp} .

$$\frac{\eta - \eta_o}{C} = \eta_{sp/c} = [\eta]_d + K' [\eta] C_d$$

Where C is the concentration. The intrinsic viscosities in decalin ($[\eta]_d$) were determined from extrapolating $\eta_{sp/c}$ versus concentration.

The temperature was controlled with heated, circulated silicone oil and the solutions were allowed to equilibrate

at the elevated temperature before flow times were measured. The possible shear rate dependence of the viscosity was neglected. Kinetic energy corrections were also considered to be negligible.

The weight average molecular weight were calculated by using an expression given by Chaing (16).

$$\bar{M}_w = \left\{ [\eta] d \times 10^4 \right\}^{1.25}$$

A summary of the general characteristics for the as recieved polypropylene resins are presented in Table II .

B. PREPARATION OF POLYPROPYLENE FILAMENTS

Melt Spinning

The initial filaments were produced by melt spinning from a screw extruder made by Fourné of West Germany. A schematic diagram of the melt spinning equipment is shown in Figure 1. The polymer pellets were fed into a 13 mm screw extruder through a seven liter hopper. The extruder supplied molten polymer to a gear pump at constant pressure. A gear pump was used to provide a constant polymer flow rate to the spinneret. The melt passed through a 325 mesh filter screen and then through a one-hole die with capillary dimensions of 0.762 mm in diameter and 3.81 mm long. There are four separate electric heating zones, provided with controllers maintained the desired temperature around the extruder and the spinning

TABLE II. AS-RECIEVED POLYMER PROPERTIES

MANUFACTURER AND CODE NUMBER	MELT INDEX grams/min	INTRINSIC VISCOSITY dl/grm	WEIGHT AVERAGE MOLECULAR WEIGHT
Diamond Shamrock (ARCO)			
5831-106-7	25	1.18	1.78×10^5
HERCULES PROFAX			
6323	12	1.99	2.36×10^5
HERCULES PROFAX			
6423	6.6	2.26	2.77×10^5

head. The molten filaments were drawn down on a feed role rotating at the desired take-up speed while they were cooled and solidified in ambient air at 23°C . The feed role was a three inch outside diameter cardboard roll mounted on a direct current driven Heller controller. The filaments were passed through a Lessona 959 constant tension winder from the feed roll where they were taken up on a 3.75 inch outside diameter take-up bobbin. Table III gives spinning conditions.

A constant melt temperature of 215°C was first selected. However difficulties in the form of distorted extrudates, were experienced for the 6323 and 6423 polymers. To reduce this problem the melt temperature of 215°C was increased to 230°C for all three polymers.

Drawing Procedure and Experimental Conditions

A broad range of 48 various drawn filaments were made using a laboratory drawing apparatus. A schematic representation of this bench scale apparatus is shown in Figure III.1. The bobbin seen in the left of Figure III.1. contains several thousand meters of continuous "as-spun" filaments. This bobbin is placed on its flat side, secured below a guide pulley located a few feet above. The fiber comes off the bobbin as required by a constant speed godet and auxiliary pulley assembly represented as godet #1 in Figure III.1. There is a hysteresis tensioner between the godet #1 and the guide above the bobbin. This tensioner imposes a predetermined

TABLE III. SPINNING CONDITIONS USED IN THE PREPARATION OF POLYPROPYLENE SAMPLES

SAMPLES	MELT T(C°)	MELT FLOW RATE (g/min)	SPINNING MEDIUM	TAKE-UP VELOCITIES (m/min)		COMMENTS
				I	II	
5831- 106-7	230	2.44	ambient	30	130	smooth spinning
6323	230	2.41	ambient	30	130	smooth spinning
6423	230	2.41	ambient	30	130	melt fracture at lower melt temperature (215 C°)

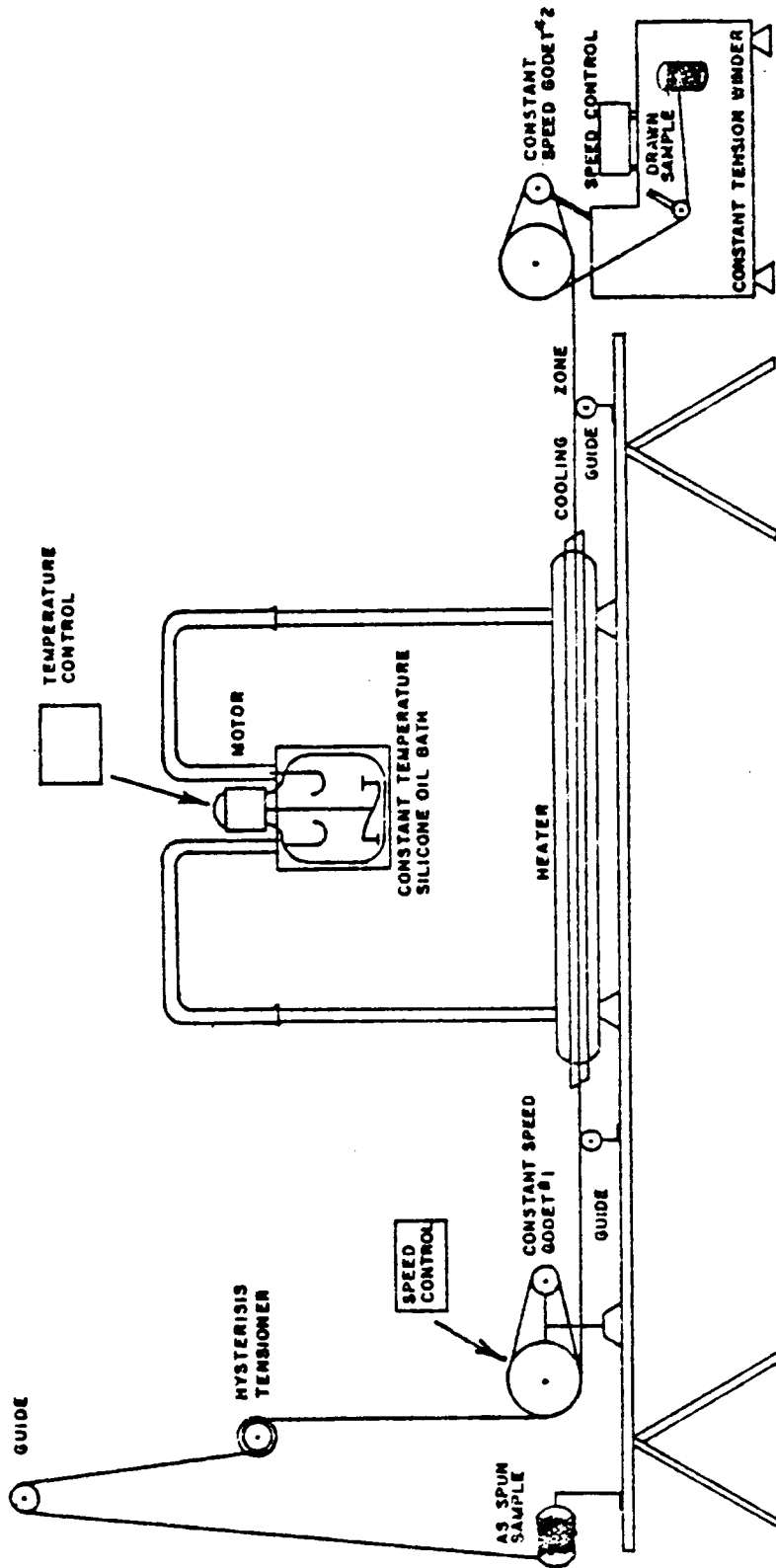


Figure III.1.1. Bench scale apparatus for drawing of polypropylene fibers.

amount of tension on the line before the filament reaches the godet #1.

The assembly referred to a godet #1 includes a constant speed motor, an auxiliary pulley, controller, and a mounting assembly and the godet itself. The godet is mounted directly on a gear reducer off the motor shaft. The auxiliary pulley is mounted on a laboratory stand together with a guiding pulley only a few inches away. The axes of rotation of the godet and auxiliary pulley are kept in the same plane. The fiber is wound several turns in this assembly and passed through the heater.

Generally, an oil heated laboratory condenser 30 cm long was used in line. The heater assembly consists of a constant temperature controller. The fiber is passed through the oil heated laboratory condenser into a cooling zone of at least two-thirds of the heater length and a guide which directs the line into the godet #2. The godet #2 assembly is shown on the right side of Figure III.1 which is a part of the winding device. It contains a constant speed motor and controller, an auxiliary pulley as with godet #1. Finally, there is a Lessona constant tension winder where the drawn fiber is wound up.

The operating procedure is a two-step process which required threading and buildup to the desired experimental conditions. The threading process is done at the operating heater temperature but with 1:1 draw ratio. The draw ratio is

a ratio of the linear speeds of the second to the first godets (V_2/V_1). First the spun fiber threaded over the guide, and on the hysteresis tensioner then follows into the constant speed godet #1. The filament must be wound at least three times around the godet assembly to assure there is no slippage or over feed during the drawing process. Next, the fiber is passed through the heater, into the second godet while it is wound four or five times around the godet. The threading process will be completed by setting the winding mechanism in motion at the corresponding speed to provide a draw ratio of 1:1.

The second step of the operating procedures is the build-up operating conditions. First of all, it is very important to make sure that the filament is making good contact with the heater surface by positioning the guides and the heater properly. The heater residence time will be a function of the draw ratio, the heater length and the fiber throughput which is solely determined by the speed of the first godet. A build up to the ultimate filament throughput may be carried out by simultaneously changing of the speeds V_1 and V_2 to keep a constant draw ratio and close to one. At these conditions the heater residence time is inversely proportional to $V - V_1 = V_2$ i.e., $\Gamma = L/V$ where L is the heater length and V is the linear speed of the filament across the system. The draw ratio is now adjusted by increasing the speed V_2 slowly to allow the winding device to follow the increase in throughput. In this

case, the system could be operating in steady state. The advantage of using such an arrangement is in the temperature control capabilities to $\pm 0.2^{\circ}\text{C}$ at 100°C and the smoothness of the surface. Each spun filament was drawn to both just beyond the natural draw ratio and secondly nearly to fracture of the filament. Table IV gives the drawing conditions.

C.CHARACTERIZATION OF SPUN AND DRAWN SAMPLES

Scanning Electron Microscopy (SEM)

An AMR model high resolution scanning electron microscope made by advanced metals research corporation was used. The principal component of this instrument given in Figure III.2. Scanning electron micrographs of peeled drawn fibers were obtained to study internal structure. Samples were prepared by use of a peeling technique (92,96,116) and mounted horizontally on aluminum sample holders over double-sided adhesive tape as shown in Figure III.3. After the samples were mounted (on mounting stools), they were electroplated with gold-palladium in a vacuum chamber. The coating of metal on the filament samples proved to be extremely important to obtain the higher magnification micrographs without "charging" of the sample.

TABLE IV. DRAWING CONDITIONS USED IN THE PREPARATION OF POLYPROPYLENE FIBERS

AS-SPUN SAMPLE	TAKE-UP VELOCITY (m/min)	DRAW TEMPERATURE (C°)				DRAW RATIO (x)
		I	II	III	IV	
5831-106-7	30	25	60	90	50	3.5, 6
	130	25	60	90	150	3.5, 6
6323	30	60	90	120	150	3.5, 6
	130	25	90	120	150	3.5, 6
6423	30	60	90	120	150	3.5, 6
	130	25	90	120	150	3.5, 6

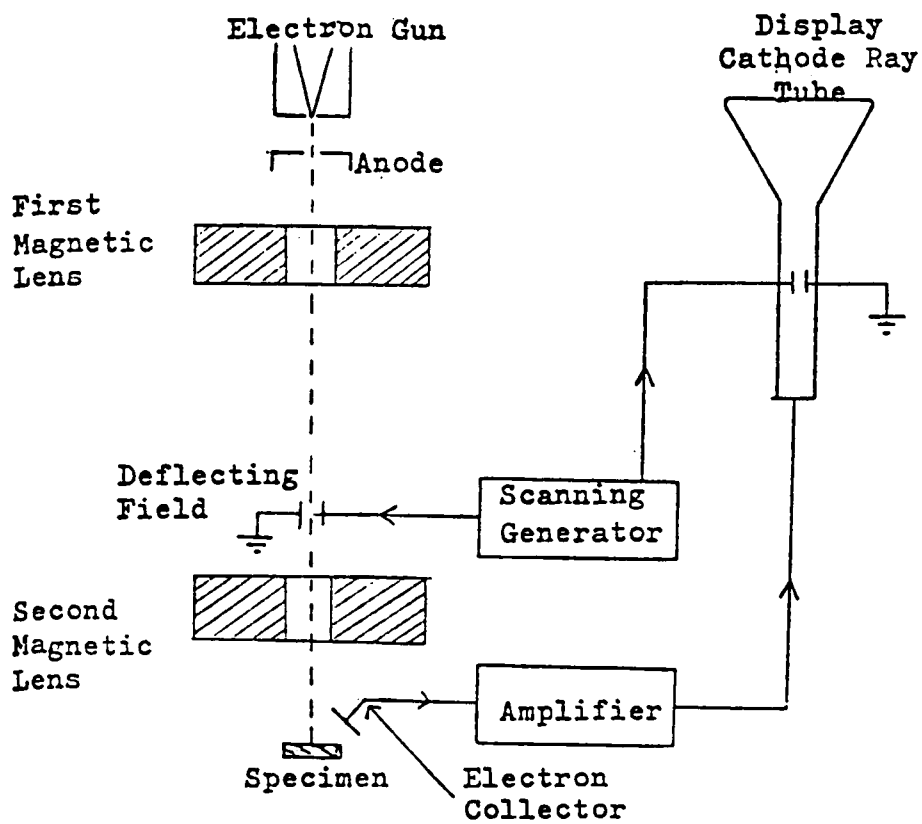


Figure III.2. Principle of the Scanning Electron Microscope.

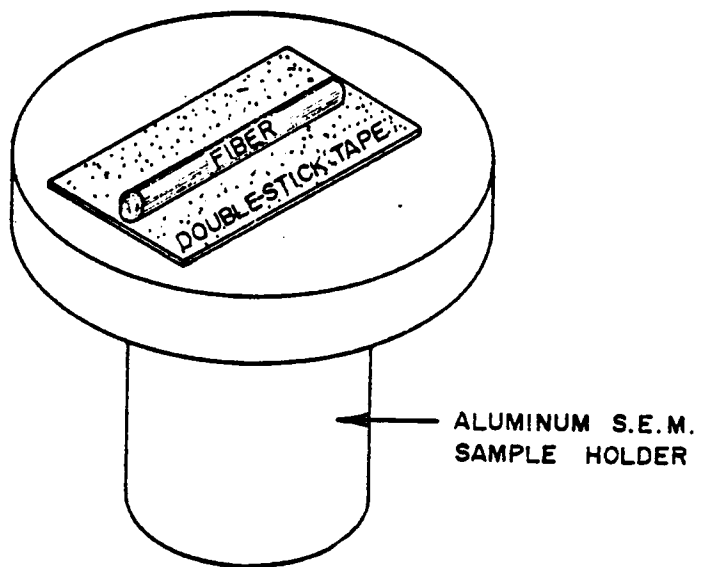


Figure III.3. SEM Sample Mounting Technique

Qualitative Wide Angle X-ray Scattering (WAXS)

Wide angle x-ray diffraction patterns for the spun and drawn samples were obtained using a Philips Norelco X-ray Generator and flat plate camera. The radiation used was in filtered copper K_{α} (wave length 1.542 Angstroms) and operating scatterings were 40 kv and 15 mA. The sample distance to film was 3.70 using a sample holder which was attached to a beam collimeter by a rubber attachment (see Figure III.4). The exposure times were varied in order to obtain relatively constant intensities for filaments with different diameters.

Quantitative Wide Angle X-ray Scattering

Expressions for the orientation factor were given in Chapter II. In this research Wilchinsky's analysis was used to determine the orientation function for monoclinic polypropylene. In this case there is no set of diffracting planes perpendicular to the c-axis which reveal the c-axis orientation directly. However, as noted in Chapter II, according to Wilchinsky's analysis the orientation factor for the c-axis (f_c) can be calculated from the values of $(\cos^2\theta)_1$ and $(\cos^2\theta)_2$ evaluated for two planes which are parallel to the c-axis.

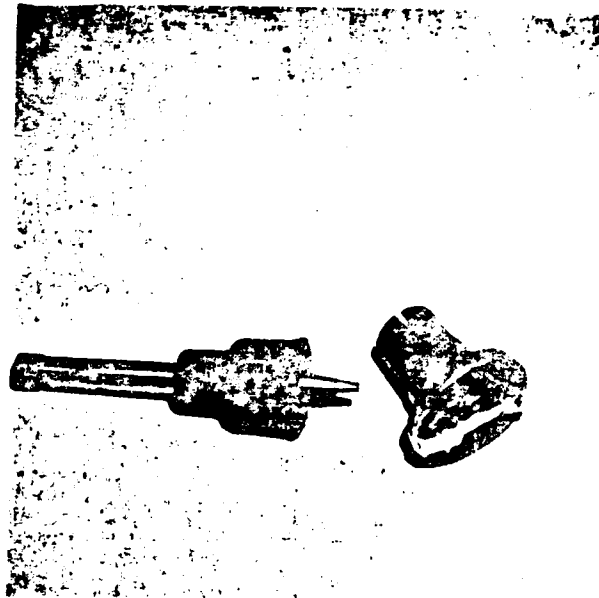


Figure III.4. Fiber Sample Holder Attachment for obtaining WAXS Patterns.

Two planes (110 and 040) were selected for use in determination of c-axis orientation. For these planes the Wilchinsky expression can be written as,

$$\overline{\cos^2 \theta_{c,z}} = 1 - \frac{(1 - \sin^2 \rho_{040}) \overline{\cos^2 \theta_{110,z}} - (1 - 2 \sin^2 \rho_{110}) \overline{\cos^2 \theta_{040,z}}}{\sin^2 \rho_{110} - \sin^2 \rho_{040}} \quad (14)$$

For a uniaxially oriented sample the average value of the square of the cosine of the angle between the fiber axis and the normal to (hkl) planes is given by,

$$\overline{\cos^2 \theta_{hkl}} = \frac{\int_0^{\pi/2} I(\theta) \cos^2 \theta \sin \theta d\theta}{\int_0^{\pi/2} I(\theta) \sin \theta d\theta} \quad (15)$$

Where $I(\theta)$ represents the relative value of the intensity for the diffracted beam at angle θ .

The numerical values of ρ_{110} and ρ_{040} were calculated from the geometry of the unit cell by Wilchinsky (120). They were found to be $\rho_{040} = 0$ and $\rho_{110} = 72.5$. Substitution of these values into Equation (14) gives,

$$(\overline{\cos^2 \theta_{c,z}}) = 1 - 1.1099 \overline{\cos^2 \theta_{110,z}} - 0.901 \overline{\cos^2 \theta_{040,z}} \quad (16)$$

The value for $(\overline{\cos^2 \theta_{c,z}})$ was obtained by substituting the experimental values $(\overline{\cos^2 \theta_{110,z}})$ and $(\overline{\cos^2 \theta_{040,z}})$ into Equation (16). The c-axis crystalline orientation function was calculated from Equation (10).

The quantitative measurement of the intensity distribu-

tion of 110 and 040 reflections as a function of the angle

α was carried out on Philips Norelco x-ray diffractometer system coupled with an ORTEC counting system. The diffraction sample was made up of a sheet of parallel fibers. Figure III. 5, III.6 shows the experimental setup. The intensity data were collected at the (110) and (040) peak positions, which were determined from a 2θ scan. The background intensity was evaluated from the analysis of the 2θ scans at $\alpha = 0^\circ$ and 90° . The intensity data were collected on a punched paper tape by a digital ratemeter and are corrected for background intensities.

The intensity data obtained at every $1.875^\circ \alpha$ angle starting from equatorial position and ending in the meridional position. The b-axis orientation was obtained directly from (040) plane reflections. For a monoclinic unit cell the orthogonality relationship does not hold. However an a'-axis orientation factor was obtained using an expression similar to Equation (10). In this case, the a'-axis is perpendicular to both the b and c axes of the monoclinic polypropylene unit cell. The a'axis is approximately 9.3° from the a-axis since the monoclinic angle differs by this much from 90° .

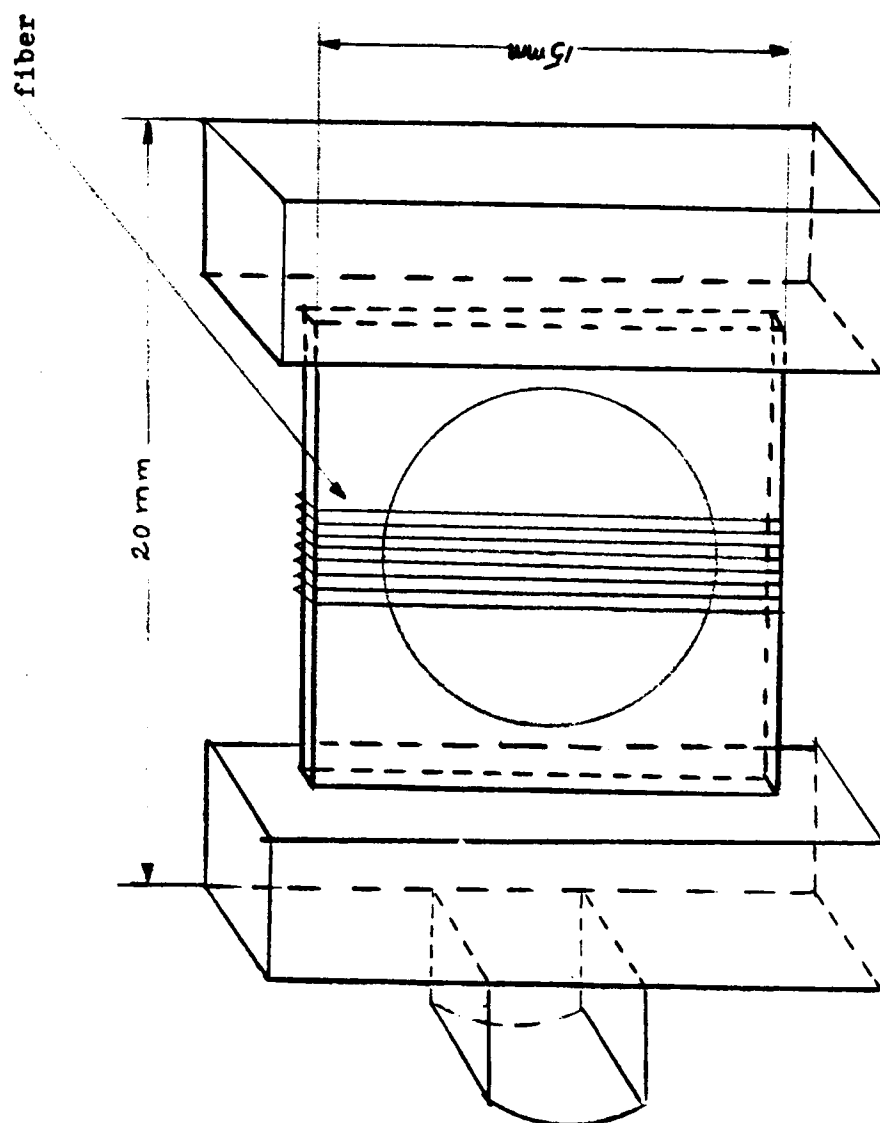


Figure III.5. Crystalline orientation sample holder

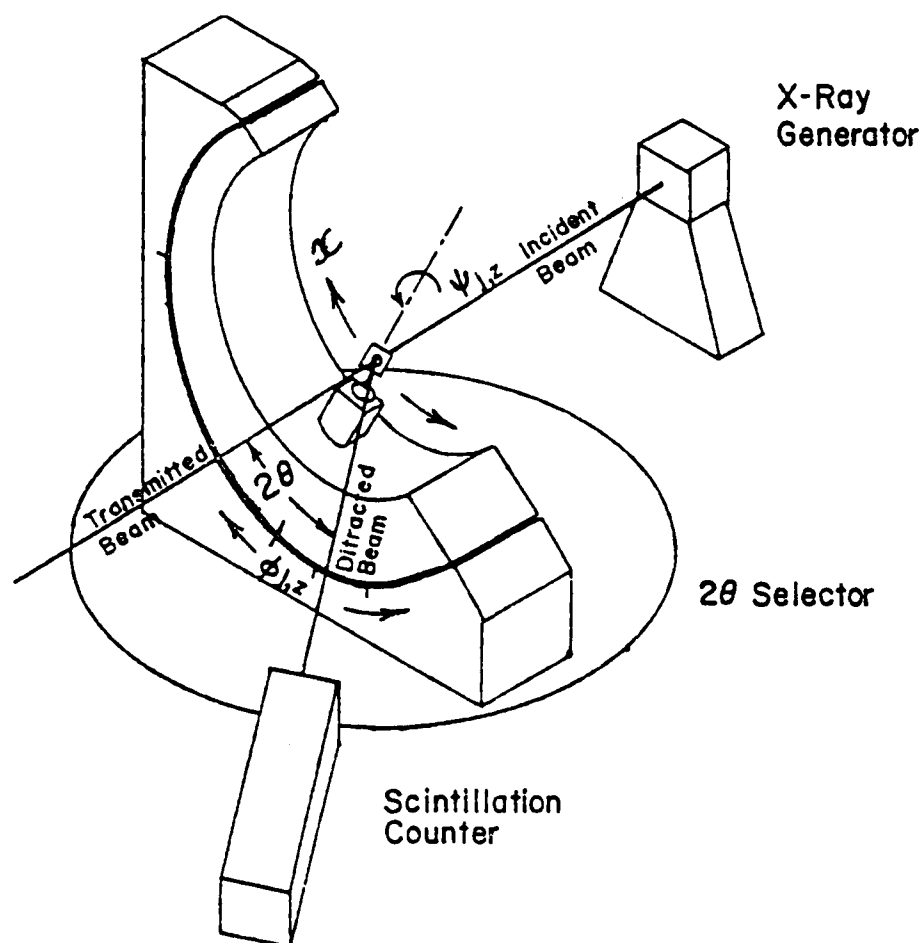


Figure III.6. Schematic arrangement of x-ray equipment for orientation factor measurements.

Qualitative Small Angle X-ray Scattering (SAXS)

Qualitative small angle x-ray patterns were obtained on spun and drawn filaments using a Rigaku General Electric Rotating Anode X-ray Generator and a modified Kiessig Camera with pin hole collimation. Patterns with a resolution of 400 Å were obtained with a custom made collimator. A mechanical vacuum pump was used to reduce air scattering effects between the filament sample and the film. The sample to film distance was 40 cm. Exposure times were varied from eighteen to twenty four hours to adjust the relative intensities for the fibers with varying diameters. The operating radiation setting for generator were 30 kv and 20 mA.

Quantitative Small Angle X-ray Scattering (SAXS)

The 10 meter small angle x-ray scattering facility of the National Center for Small Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory was used to quantitatively measure intensity profiles and integrated intensities this allowed us to quantitatively investigate void number density, size distribution and shape as well as microfibril diameters as a function of spinning and drawing variables.

A schematic of the 10 meter SAXS is shown in Figure III. 7. The operation of the 10 meter SAXS camera is via computer

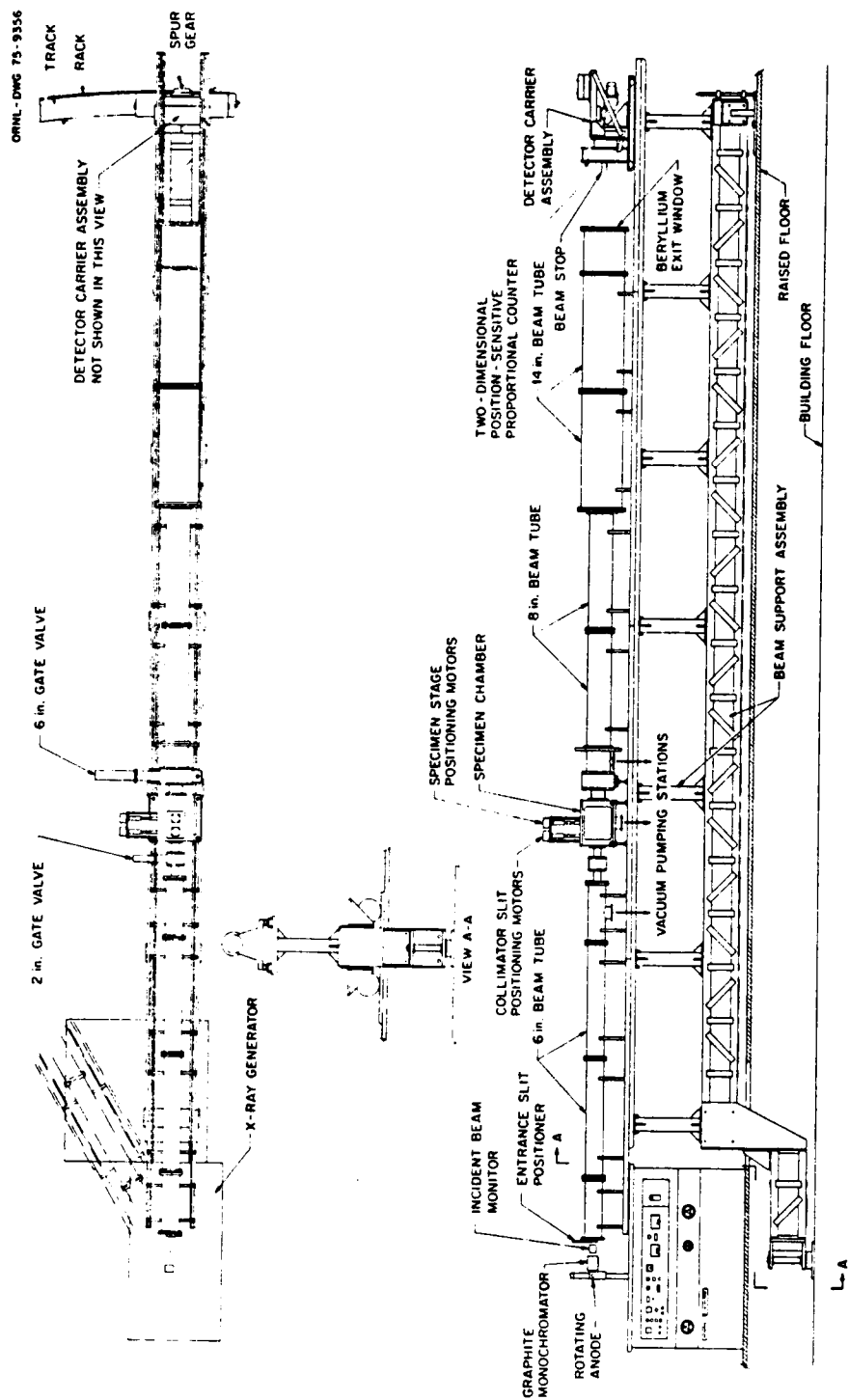


Figure III.7. Diagram of 10 meter small angle x-ray scattering.

program called SAX. Generally, SAX is activated with the input and output assignments to the LSI terminal that is directly connected to the Modcomp computer. The camera utilizes a rotating anode x-ray source, crystal monochromatization of the incident beam, pin-hole collimation, and a two-dimensional position sensitive counter. The focal spot-to-sample and sample-to-detector distance were set at 5 meter to obtain a system resolution of 4.0 mrad. The size for a specimen of 0.1 cm X 0.1 cm (fixed) and the incident wavelength was $1.542 \text{ \AA}$ ($\text{CuK}\alpha$). Each sample was made up of a sheet of parallel fibers (see Figure III.6) and fixed on a specimen holder which was mounted on the specimen chamber. The detector area of resolution elements was 64 X 64 mm. The X-ray generator voltage and current were operated at 40 K_V and 30 mA respectively. A glassy carbon was used in order to measure the sample transmission. Air scattering was reduced by evacuating the camera with a mechanical pump.

The data were recorded in the memory of a minicomputer by a high speed interface which uses a microprocessor to map the position of an incident photon into an absolute minicomputer memory address. The data recorded in the computer memory were processed on-line by a designed program with background and detector sensitivity corrections.

Density and Crystallinity

The densities of the spun and drawn filaments were determined using a distilled water-isopropyl alcohol density gradient column at 25°C. A technique described by Tunr et al (114) and Wiley (119) constructed to create a linear density column by continuous mixing of a heavy and a light solution. Two solutions, a more dense one (A) and a less dense one (B), are kept in equal volume communicating vessels while a steady stream of the heavy liquid is continuously drawn to fill the column. The pressure differential caused by the depletion of solution (A) causes fluid to flow from the liquid (B) to the heavy solution (A) contained. If the more dense side is kept well mixed, as the density gradient column is being filled, a linear gradient will result as a consequence of the linear variation of the density in vessel (A) with time.

The spun and drawn filaments were added into the column for approximately twenty four hours to seek their final level of displacement. In the absence of voids the fraction of crystallinity can be determined from the experimental density and the following expression (40).

$$\bar{X} = \frac{\rho_c (\rho - \rho_{am})}{\rho (\rho_c - \rho_{am})} = \frac{\frac{1}{\rho} - \frac{1}{\rho_c}}{\frac{1}{\rho_{am}} - \frac{1}{\rho_c}} \quad (17)$$

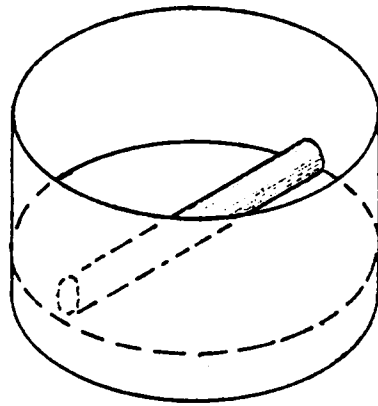
Where ρ is the measured experimental density, ρ_c and ρ_{am} are hypothetical 100 percent crystalline and amorphous

sample respectively. The crystal density ρ_c can be calculated from the known unit cell structure and unit cell monomer molecular weight, while the amorphous regions density ρ_{am} is obtained from measurements on the pure amorphous polymer or by extrapolation of the density temperature curve of the melted polymer (90).

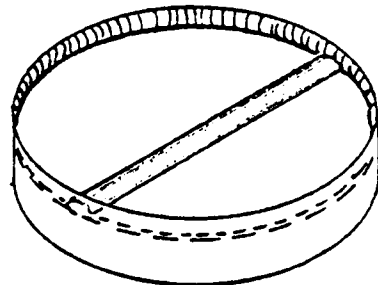
The 100 percent crystalline sample and amorphous sample were assumed to have densities of 0.932 and 0.854 respectively (13).

Heat of Fusion

A model DSC-2 Perkin Elemer Differential Scanning Calorimeter was used to measure the heat of fusion for spun and drawn polypropylene samples. Small amount of polypropylene fiber were cut and sealed in the DSC holders which are highly thermal conductive supplied for calorimetry. The "standard" sample pan crimper crimps a pan cover on the pan containing the sample. Figure III.8. is shown a sketch of a pan before and after crimping. As a reference sample tin with melting point of 231.88°C and heat of fusion 14.45 cal/g were selected. A temperature range of 330°K as lower limit and 550°K as higher limit were set while the cooling and heating rate were 320 and 40 degree per minute respectively. A planimeter was used to measure the area under the curve and was converted to calories by the following expression



BEFORE



AFTER

Figure III.8. DSC Aluminum Sample Holder
(Before and After Crimp Sealing).

$$(17), \quad \Delta H \text{ (calories)} = \frac{\text{heat of fusion of standard} \times \text{weight of sample} \times \text{standard peak area}}{\text{standard fusion peak area}} \quad (18)$$

The percent crystallinity was determined using the equation of,

$$\%X = \frac{\Delta H_f}{\Delta H_f^*} \quad (19)$$

Where ΔH_f is cal/gr of sample and ΔH_f^* is a heat of fusion of a hundred percent crystalline polypropylene ΔH_f^* was assumed to be 49.95 cal/gr (10).

Birefringence

The total birefringence for the spun and drawn samples was determined using an Ortholux Polarizing Microscope with a Leitz Berek Compensator and Filar eyepiece, see Figure III. 9. A compensator of order ten was used to determine the phase difference or retardation (Γ) between two mutually perpendicular plane polarized light waves emerging from the sample. The filar eyepiece was used to measure the fiber diameter at the same time. The phase difference is proportional to the birefringence of the sample.

The experimental procedure suggested by the manufacturer of compensator was followed in determining the phase difference or retardation. Total birefringence was calculated using the following expression,

$$n = \frac{\Gamma}{d} \quad (20)$$

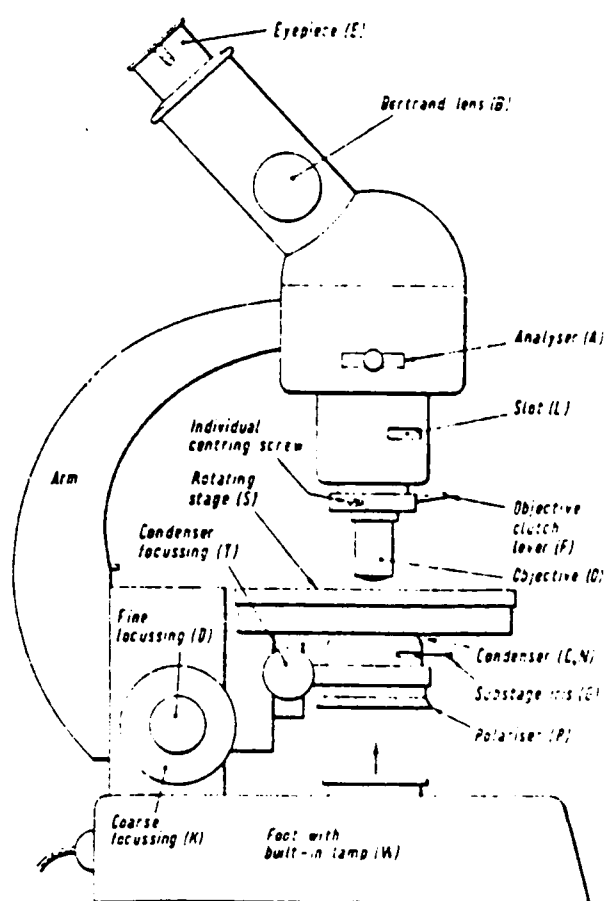


Figure III.9. Polarizing microscope.

Where Γ is the retardation and d is the fiber diameter.

D. TENSILE MECHANICAL PROPERTY MEASUREMENTS

The tensile properties of all the spun and drawn filaments were obtained at room temperature with a table model Instron Tensile Testing machine. The Instron Tensile tester applies a force to the sample and this force is monitored as a function of time on the recorder. Figure III. 10 shows a fiber clamped between the tester grips being pulled as the cross head moves upward. Force versus elongation curves were obtained for all the filaments and the results were converted to evaluate the Young's modulus, tensile strength and percent elongation to break.

The strain on the sample (γ) was determined from the following equation,

$$\gamma = \frac{\Delta L}{L_0} = \frac{(\text{cross head speed}) \times (\text{chart distance})}{(\text{chart speed}) \times L_0} \quad (21)$$

Where L_0 is the original length of the filaments. The engineering stress was calculated from the expression,

$$\sigma = \frac{F}{A_0} \quad (22)$$

where F is the force and A_0 is the original cross section area of the fiber. Elastic modulus (ϵ) is given by the following equation,

$$\epsilon = \frac{\sigma}{\gamma} \quad (23)$$

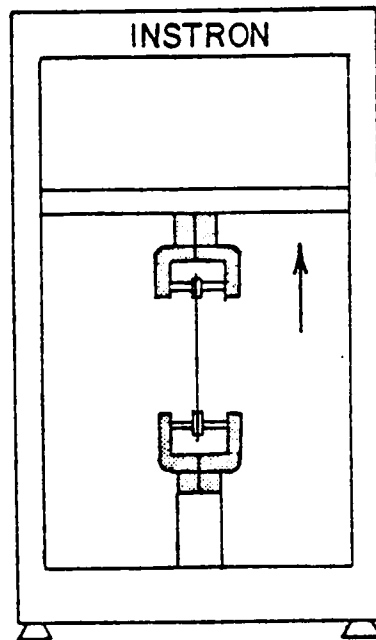


Figure III.10. Fiber being pulled on the Instron Tensile Tester.

his was calculated from initial slope of the force time curve obtained from the recorder.

The percent elongation to break also was determined using the expression,

$$\% \text{ Elongation to Break} = \frac{L_f - L_o}{L_o} \quad (24)$$

Where L_f is the length at fracture and l_o is the initial gauge length. All of the filaments were tested with a gauge length of 2 cm, cross head speed of 50 mm/min, and chart speed of 5 inch/min. The reported data were obtained by averaging five tests on each filament.

CHAPTER IV

STRUCTURE DEVELOPMENT IN MELT SPUN AND DRAWN FIBERS

As mentioned in Chapter III, three polypropylenes having different molecular weights and from two different suppliers were spun at a single extrusion temperature of 230°C.

The spinnability decreased with increasing molecular weight at extrusion temperature of 215°C. This was especially evident for polypropylene 6423 (highest molecular weight specimen among the others with a melt index of 6.6), where melt fracture was observed. In order to avoid melt fracture, it was required to increase the extrusion temperature from 215°C to 230°C.

The differences between Hercules and Diamond Shamrock polymers probably could be traced to differences in molecular weight distribution. It is possible that the high melt index 106-7 polymer is visbroken in order to produce the high melt index. This would also narrow the molecular weight distribution. The latter effect may be responsible for the observed differences in spinnability.

A. CHARACTERIZATION OF MELT SPUN FILAMENTS

Qualitative Characteristics

Figure IV.1 shows wide angle x-ray patterns (WAXS) of polypropylene filaments spun into ambient air with two different take-up velocities. It can be seen that all of the spun fibers have a well formed highly crystalline monoclinic or α -form crystal structure. The filaments which were formed by melt extrusion with low extensional stress at the time of crystallization are characterized by a low orientation as judged by the wide angle x-ray patterns. The four rings, from inner reflection to the outer reflection, are the 110, 040, 130 and 111 reflections (70).

It is also clear from Figure IV.1 that the samples spun with take-up velocity of 30m/min have a lower level of crystalline orientation than the samples of the same polymers spun at a take-up velocity of 130 m/min, comparing a,c, and e to b, d, and f.

The effects of the molecular weight on orientation are also shown quantitatively in Figure IV.1. Comparing the WAXS patterns in Figure IV.1, a, c, and e for 5831-106-7, 6323, and 6423 respectively with take-up velocity of 30 m/min there seems to be a noticeable decrease in the 110 and 130 azimuthal arc length with increasing molecular weight indicating an increase of orientation.

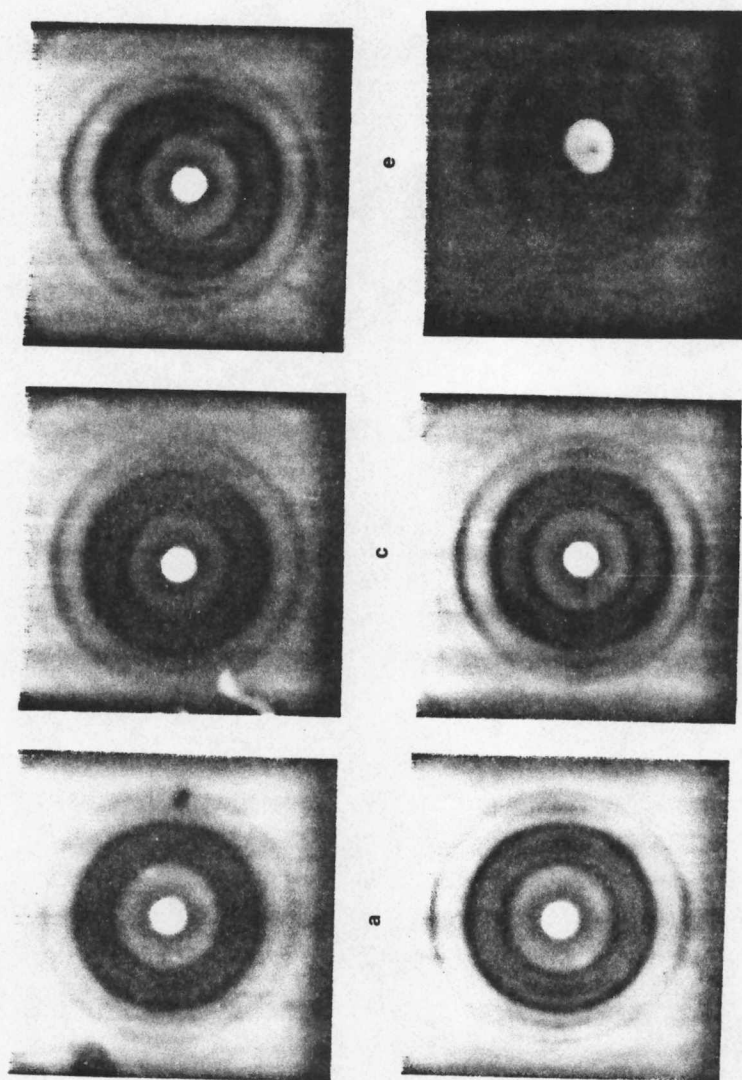


Figure IV.1.1. WAXS patterns of melt spun polypropylene fibers.

- (a) 106-7, Take-up velocity 30m/min
- (b) 106-7, Take-up velocity 130 m/min
- (c) 6323, Take-up velocity 30 m/min
- (d) 6323, Take-up velocity 130 m/min
- (e) 6423, Take-up velocity 30 m/min
- (f) 6423, Take-up velocity 130 m/min

Figure IV.2 shows the small angle x-ray patterns of spun polypropylene filaments. The SAXS patterns of filaments spun at take-up speed of 30 m/min exhibit a continuous ring of nearly uniform intensity Figure IV.2 a,c,e. These are the same conditions which lead to low orientation in the WAXS patterns Figure IV.1 a,c,e. By increasing the take-up velocity to 130 m/min the SAXS patterns evolve to approximately two point patterns Figure IV.2, b,d,f.

In the next three sections the results of quantitative measurements of crystallinity and orientation are presented.

Crystallinity

As noted in Chapter III, the percent crystallinity of polypropylene samples was determined at 25°C using a distilled water-isopropyl alcohol density gradient column and also from a model DSC-2 Perkin Elmer Differential Scanning Calorimeter.

Table V gives the percent crystallinity values in the spun fibers as a function of the take-up velocity for each method. It can be seen from these values that the absolute values of the crystallinity levels are slightly higher for the samples which were spun with a take-up speed of 130 m/min than those spun with a take-up velocity of 30 m/min. However, an interesting trend in the crystallinity levels with molecular weight was also observed, particularly by comparison

TABLE V. PERCENT CRYSTALLINITY FOR MELT SPUN POLYPROPYLENE FIBERS

SAMPLE	TAKE-UP VELOCITY m/min	METHODS- DENSITY GRADIENT COLUMN	DSC
6423	130	56.81	51.09
6423	30	55.11	50.3
6323	130	55.62	50.31
6323	30	54.40	49.08
5831- 106-7	130	52.28	46.76
5831- 106-7	30	50.34	44.48

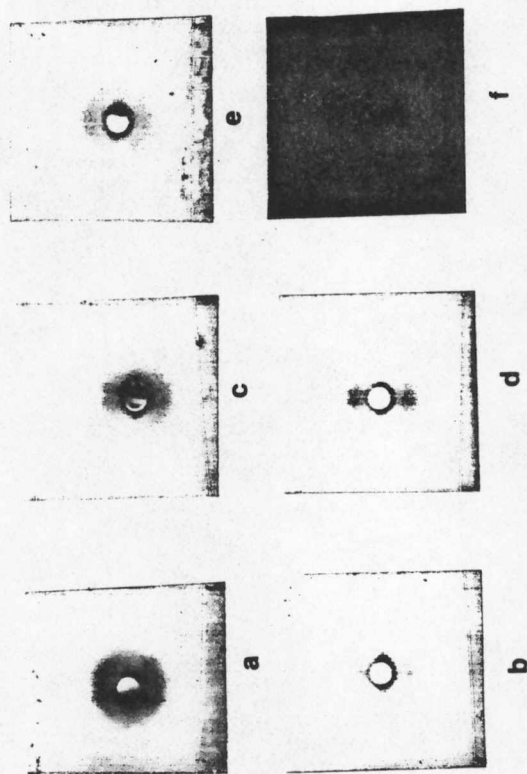


Figure IV.2. SAXS pattern for melt spun polypropylene filaments.

- (a) 106-7 with take-up velocity 30 m/min
- (b) 106-7 with take-up velocity 130 m/min
- (c) 6323 with take-up velocity 30 m/min
- (d) 6323 with take-up velocity 130 m/min
- (e) 6423 with take-up velocity 30 m/min
- (f) 6423 with take-up velocity 130 m/min

of 6423 ($M = 2.77 \times 10^5$) and 5831-106-7 ($M_w = 1.78 \times 10^5$). The crystallinity increased slightly with increasing molecular weight. Since the crystallinity levels for specimens from different manufacturers differed more than between the two Hercules Profax having different molecular weight, some of this variation may be a result of different tacticity produced by different catalyst systems or levels of success in extrusion of the atactic polymer.

As it appears, from Table V, there is a slight difference in measured crystallinity levels using the two different techniques. The absolute values of crystallinity levels for melt spun polypropylene filaments using density gradient column were found to be 10 percent higher than the crystallinity values which were determined from D.S.C. method. This difference probably is associated with errors in theoretical densities of 100 percent amorphous polypropylene, the heat of fusion of crystalline polypropylene as well as experimental errors of measurement of the density and heat of fusion of the samples.

Crystalline Orientation Functions

Table VI gives the values of Hermans-Stein crystalline orientation factors (f_c, f_b, f_a) for melt spun isotactic polypropylene as a function of take-up velocity. The value of f_c increases with take-up velocity which indicates that the

TABLE VI. CRYSTALLINE ORIENTATION FACTORS FOR MELT SPUN POLYPROPYLENE AT
VARIOUS TAKE-UP VELOCITIES

SAMPLE TAKE-UP VELOCITY m/min		f_c	f_b	f_a
6423	130	0.48	-0.26	-.022
6423	30	0.43	-0.23	-0.2
6323	130	0.46	-0.25	-0.21
6323	30	0.42	-0.23	-0.19
5831- 106-7	130	0.38	-0.21	-0.17
5831- 106-7	30	0.33	-0.18	-0.15

c-axes are tending to become more aligned with the fiber axis, with increasing take-up speed. The b-axis orientation function (f_b) values decrease with increasing take-up velocity which indicates a tendency for perpendicular alignment of the b-axis with the fiber axis. The f_a values also decrease slightly with increase in the take-up speed. The a- axis is approximately 9.3° from the true a-axis since the β -monoclinic angle differs by this much from 90° . The effects of the molecular weight on the orientation functions can also be seen. Higher molecular weight samples exhibited higher f_c values at any given take-up speed. The effect of tacticity, if any, on f_c is not clear from these results.

Birefringence

The measured birefringence is an indicator of average molecular orientation in the samples. The crystalline orientation function discussed earlier, refer to the crystalline phase of the samples. On the other hand, it was mentioned that these polypropylene fibers are significantly less than one hundred percent (about 50 to 55 percent) crystalline. This suggests also the importance of orientation in the amorphous regions.

Table VII gives the values of birefringence for the melt spun fibers. The variation of birefringence as a function of take-up velocity and molecular weight can be seen from

TABLE VII. BIREFRINGENCE FOR MELT SPUN POLYPROPYLENE FILAMENTS

SAMPLE	TAKE-UP VELOCITY m/min	t (m m)	Δn (m μ)	f _{am}
6423	130	0.1710	15×10^{-3}	0.23
6423	30	0.1899	11.2×10^{-3}	0.20
6323	130	0.1720	13×10^{-3}	0.22
6323	30	0.1999	9×10^{-3}	0.20
5831- 106-7	130	0.1691	8.8×10^{-3}	0.18
5831- 106-7	30	0.1780	6.1×10^{-3}	0.16

this table. The birefringence increases with take-up velocity. At any given take-up speed fibers with higher molecular weight exhibit higher values of birefringence. Both the crystalline and amorphous orientation factors for melt spun polypropylene have been previously studied by Nadella et al (65). They reported that the orientation development in the amorphous region is always less than the orientation in the crystalline regions. Also both the amorphous and crystalline orientation factors increase with increasing spinline stress.

The amorphous contributions to overall orientation was calculated by applying the experimental crystallinity and birefringence together with intrinsic birefringence for amorphous and crystalline polypropylene given by Samuels (90) to the equation (12).

The values of f_{am} for spun fibers are presented in Table VII. The value of f_{am} increases with increasing take-up velocity and molecular weight of polypropylene. The later effect is not significant from comparison of Profax 6323 (melt index 12) and 6423 with melt index of 6.6.

Discussion of Melt Spun Filaments

As noted in the first section of this chapter, the polypropylene filaments were spun into ambient air. WAXS and SAXS patterns revealed that these fibers are highly crystalline and the crystallinity values were similar to the values obtained by Sheehan and Cole (91), Samuels (90),

Henson (37), and Nadella et al (65).

The development of morphology in the spinline of melt spun polypropylene can be followed with the increase in birefringence and crystalline orientation with spinline stress. The effect of the other spinline variables, such as; molecular weight, flow rate, melt temperature, and take-up velocity also may effect the development of morphology in independent ways. But as seen in previous research for polyethylene, polypropylene, polystyrene, Nylon 6 and polyester (51,66,71,34) the combination of all these influences on morphology can be traced to their effect on spinline stress.

The development of morphology with increasing take-up velocity can be partially followed through SAXS patterns Figure VI.2. At low take-up velocity (30 m/min) the SAXS patterns show an indication of a nearly unoriented lamellar superstructure probably a spherulitic structure. Samuels (90) observed spherulitic morphology in transmission electron microscope (TEM) replicas of spun polypropylene. By increasing the take-up velocity (130m/min), the ring of SAXS patterns appears to change from continuous nearly uniform intensity into a nearly two-point patterns. This suggests, an increase of orientation of lamellar superstructure. In addition this interpretation in polypropylene is supported by TEM observation of lamellae stacked parallel to the fiber axis by Fung, et al (29).

The morphology in polypropylene is complicated by bimodal orientation. The presence of bimodal distribution of unit cell orientations makes polypropylene unique. This phenomenon has been considered by Clark (20), Clark and Spruiell (120), and Anderson and Carr (42). Clark and Spruiell (20) proposed a morphological model for bimodal orientation of polypropylene. This model for flow crystallized polypropylene is applicable at high spinline stresses, where two point patterns of SAXS are obtained. In the development of this model, it was assumed that crystallization proceeds in two stages. From some sort of fibril nuclei a row structure of planar lamellae develops; then the lamellae grow with the growth axis of the lamellae parallel to the a-axis of the unit cell. During this primary crystallization, some molecules are rejected from the growing lamellae into regions between them. At a short time later in a secondary stage of crystallization these molecules crystallize. In this secondary population the orientation of the crystals is presumably controlled by an epitaxial matching between the $13 \text{ \AA}$ repeat of the polypropylene molecule and the fold surface of the primary crystals. This matching requires that the chain axis of the secondary component be perpendicular to the chain axis of the primary component. The proposed interpretation of bimodal orientation consists of a row structure of planar lamellae interconnected by tie molecules, which gives rise to the c-axis oriented contributions together with small interlamel-

lar crystals in the a-axis orientation (90).

The effect of molecular weight on crystalline orientation function and morphology was generally similar to the results obtained by Nadella et al (65).

B. DSC CRYSTALLINITY OF DRAWN FILAMENTS

Figure IV.3 is a plot of percent crystallinity (which was measured directly from the heat of fusion of samples) versus temperature of drawing. It can be seen that the crystallinity increases slightly with increasing draw temperature. The effect of draw ratio on the crystallinity of the samples, at given take-up velocity as melt spun, are also shown in this figure. The samples which were drawn at higher draw ratio (Draw Ratio =6X) show significantly higher values of crystallinity at any given draw temperature.

In comparing Figure IV.3 with Figure IV.4 the effects of take-up velocity of drawn samples on crystallinity can be ascribed. At any given draw ratio and draw temperature, the drawn samples with higher take-up speed as melt spun exhibit a higher degree of crystallinity. These results are also supported by measurement of crystallinity from density gradient column in this research. The discussion of density and crystallinity measurements by density gradient column will be presented in the later section of this chapter.

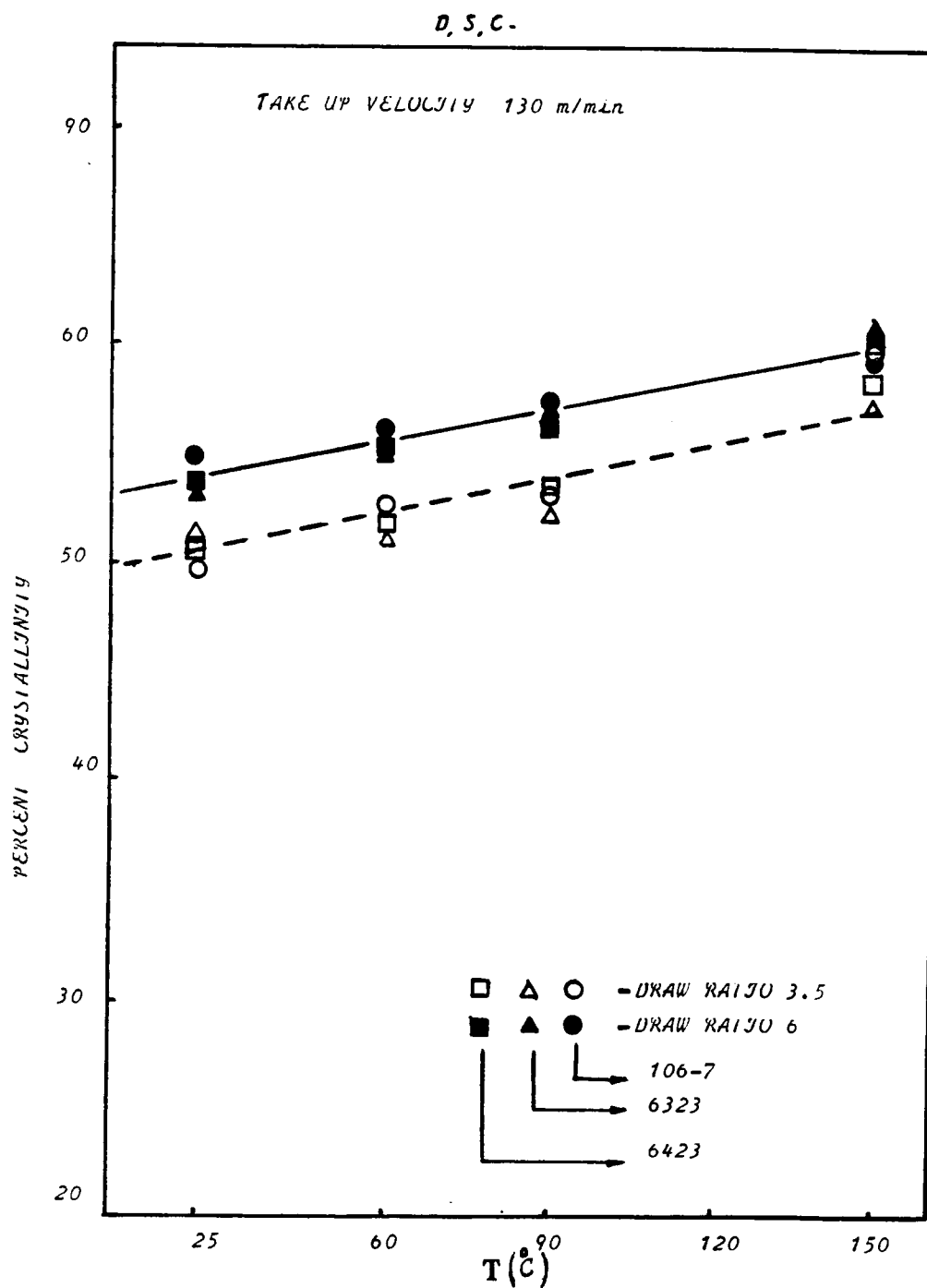


Figure IV.3. Percent crystallinity measured from DSC vs draw temperature for drawn polypropylene fibers (take-up velocity 130 m/min)

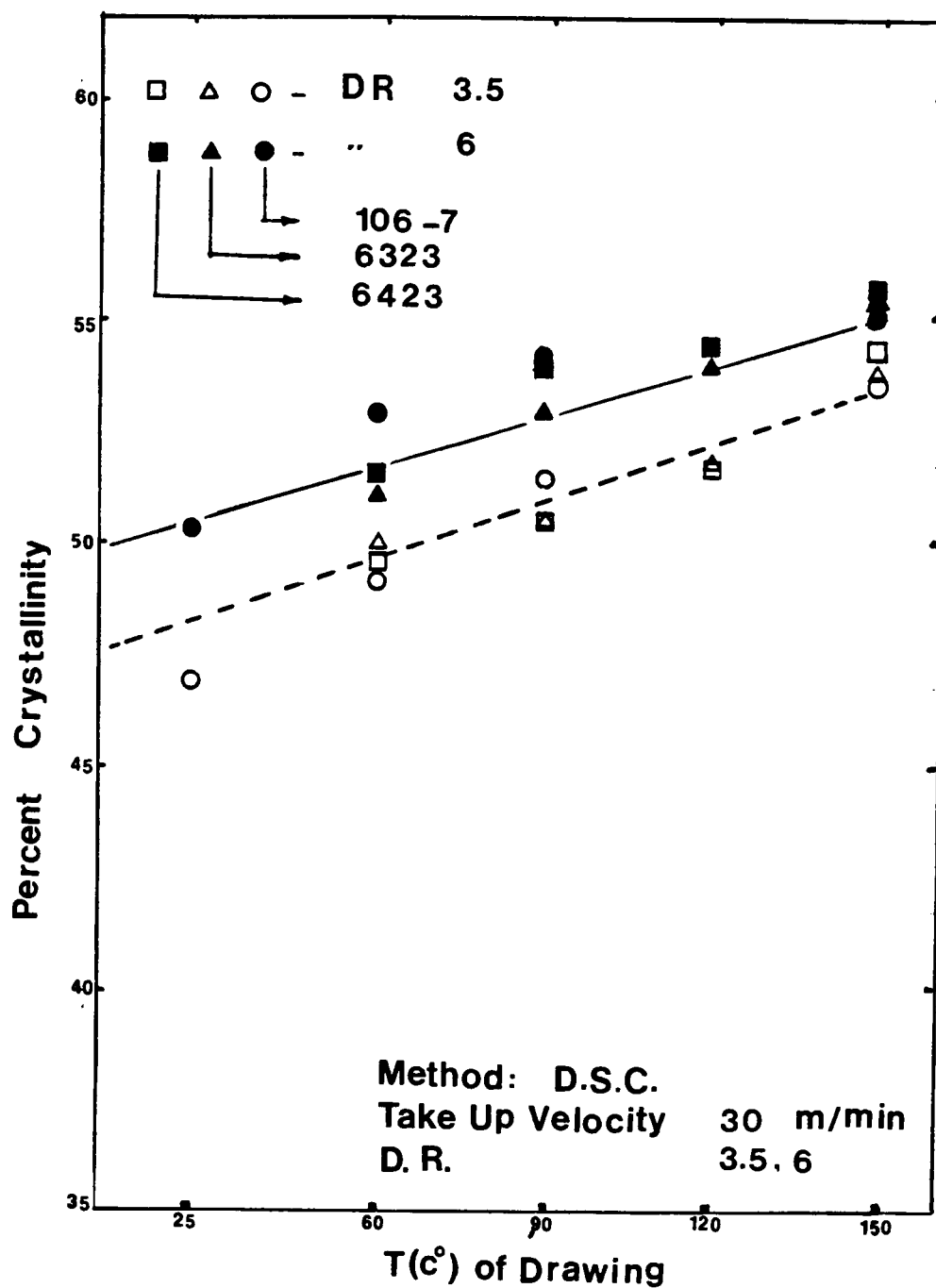


Figure IV.4. Percent crystallinity measured from DSC vs draw temperature for drawn polypropylene fibers (Take-up velocity 30m/min)

C. ORIENTATION OF DRAWN FILAMENTS

Wide Angle X-ray Diffraction (WAXS)

A qualitative estimate of the degree of c-axis crystalline orientation with respect to the filament axis can be determined from the azimuthal arc length of the equatorial reflections as observed in wide angle x-ray diffraction.

Figure IV.5 shows the typical WAXS patterns of melt spun and natural drawn filaments. The WAXS pattern of the melt spun sample consists of four sharp monoclinic diffraction rings which indicates a low c-axis orientation. The WAXS patterns of the drawn filament shows very short reflections arcs, which indicate a very high c-axis orientation in the filament axis direction.

The effects of draw ratio on orientation can be seen in Figure IV.6. By increasing the draw ratio the arcs in the pattern become sharper and shorter. This again reflects the increasing of c-axis orientation. For all of the samples, high orientation were observed at higher draw ratio ($DR=6X$) compared to lower draw ratio ($DR=3.5$). There seem to be a decrease in the crystallite size as indicated by the broadening of the WAXS equatorial reflections. This feature is more pronounced in the cold drawn samples. The filaments taken-up with higher take-up velocity during the melt

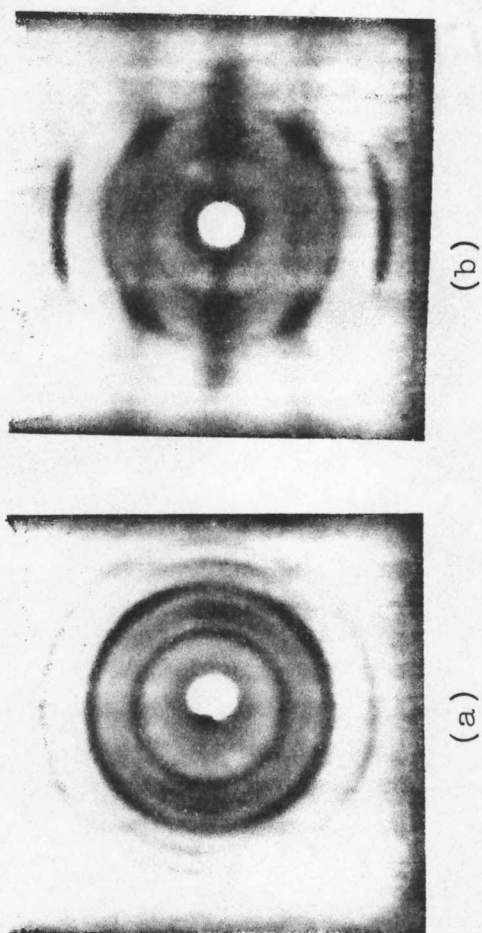


Figure IV.5. WAXS patterns of 6323
(a) as-spun
(b) cold drawn 60°C

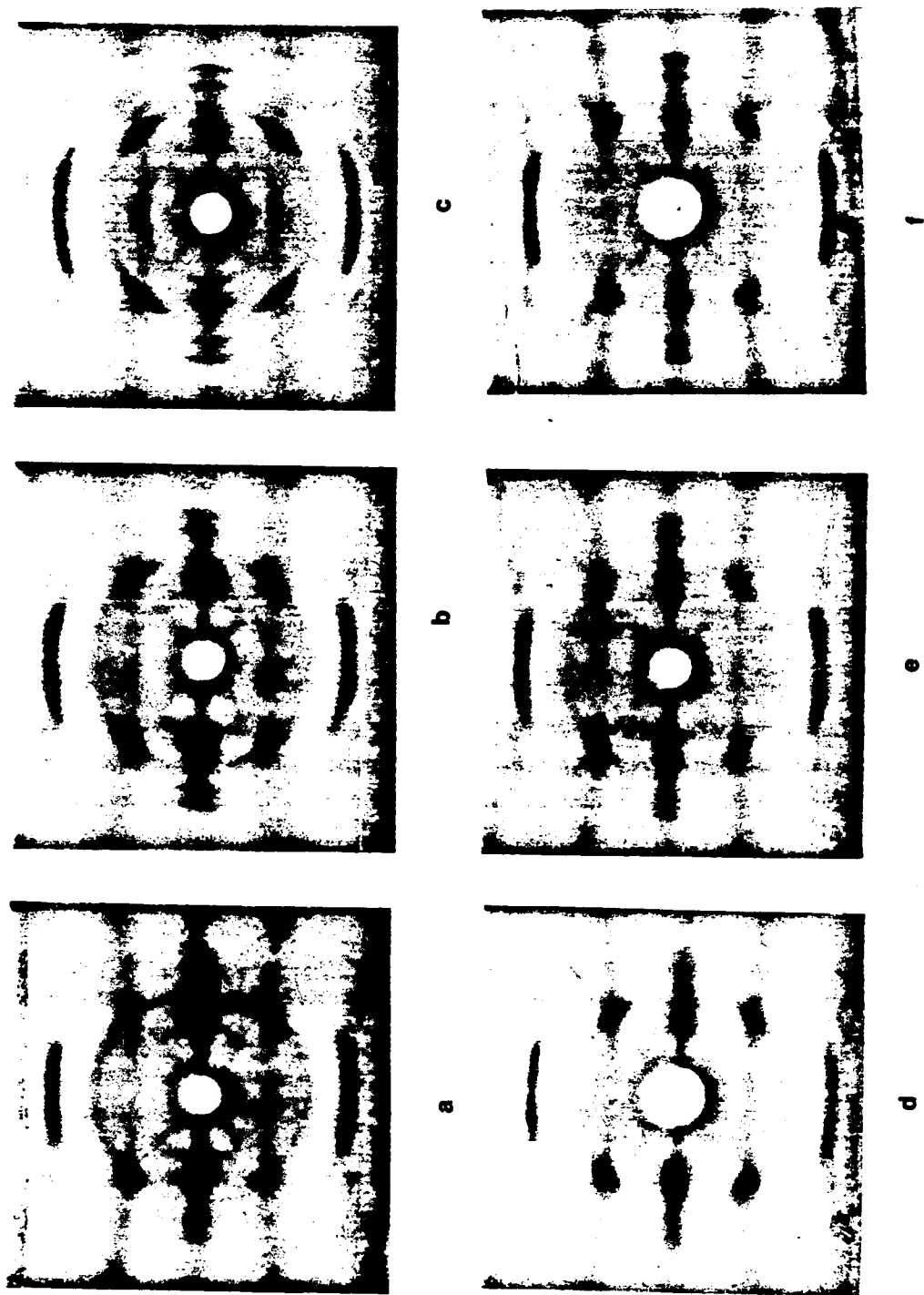


Figure IV.6. WAYS patterns of drawn 6423 with take-up velocity 130m/min
 (a-c) D.R. = 3.5, (a) $T_d = 25^\circ\text{C}$, (b) $T_d = 90^\circ\text{C}$, (c) $T_d = 150^\circ\text{C}$
 (d-f) D.R. = 6, (d) $T_d = 25^\circ\text{C}$, (e) $T_d = 90^\circ\text{C}$, (f) $T_d = 150^\circ\text{C}$

spinning show higher c-axis crystalline orientation. This is represented in Figure IV.7 for the polypropylene 6323 draw ratio 6 as a function of draw temperature.

Figure IV.8 shows WAXS patterns for selected melt spun, cold and hot drawn samples. From comparison of Figure IV.8-a with Figure IV.8-b since the x-ray data are richer in the oriented monoclinic crystalline state than in the disordered (smectic) state where is an indication of line broadening, it can be said that the crystal structure has been transformed from monoclinic type to smectic form. Figure IV.8-c shows that the samples possess highly oriented monoclinic structure as a result of hot drawing (150°C).

A careful observation of the moderately oriented hot drawn polypropylene ($\text{DR}=3.5$, $T=150^{\circ}\text{C}$) Figure IV.6-c indicate the presence of a bimodal distribution of the unit cells. The spot marked "1" on Figure 6-c is associated with the a-axis oriented component of the bimodal orientation. On drawing to a higher draw ratio the a-axis component of the bimodal distribution is no longer observed. It is assumed that it is gradually destroyed by the plastic deformation of drawing.

Figure IV.9 shows WAXS patterns for 5831-106-7 (melt index 25) for 6423 (melt index 6.6). It can be seen from these patterns that for any given draw ratio and draw temperature the higher molecular weight polymer exhibits higher degree of orientation.

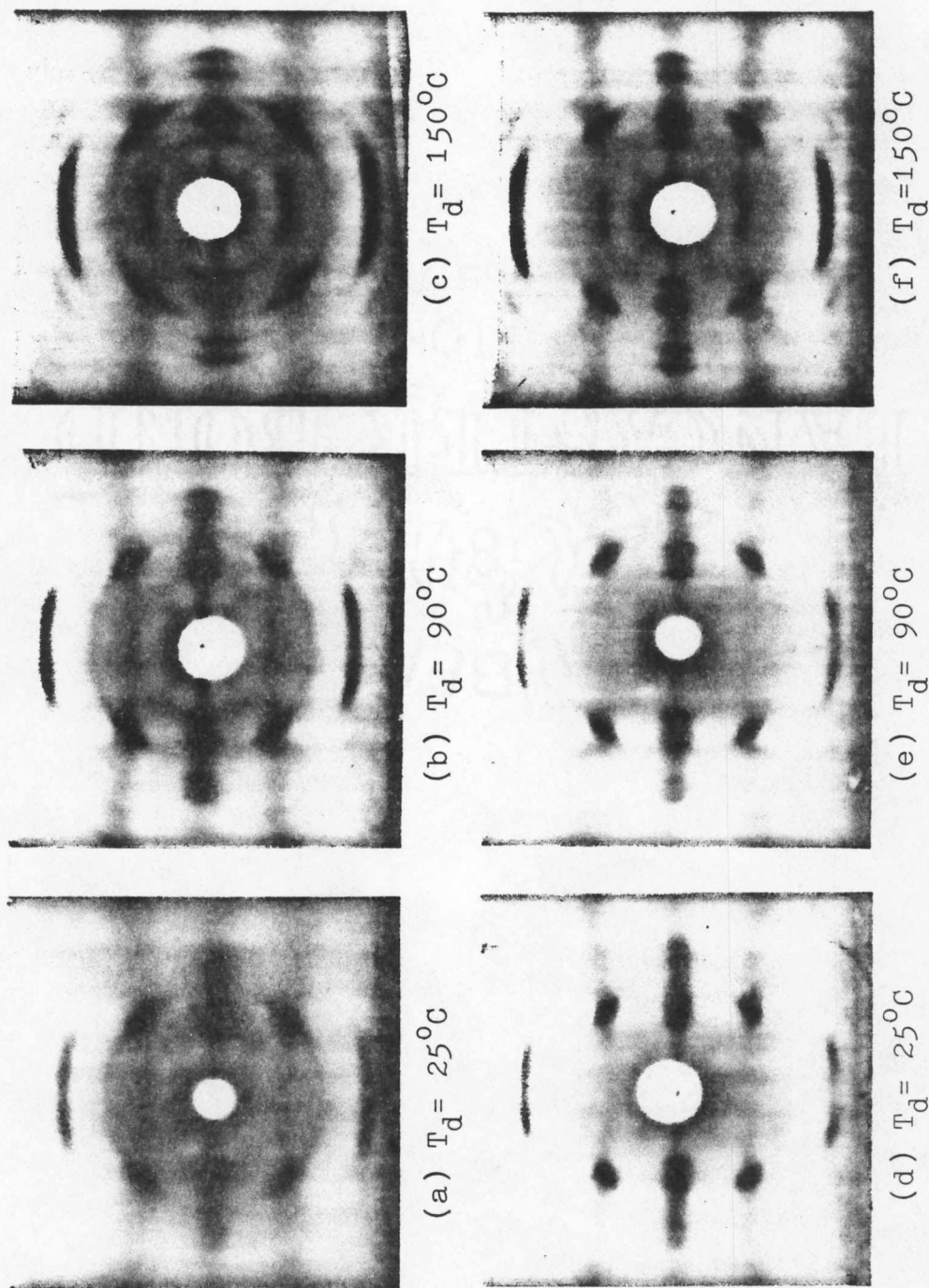


Figure IV.7. WAXS patterns of 6323, DR=6X.
 (a,b,c) Take-up velocity 30m/min
 (d,e,f) Take-up velocity 130m/min

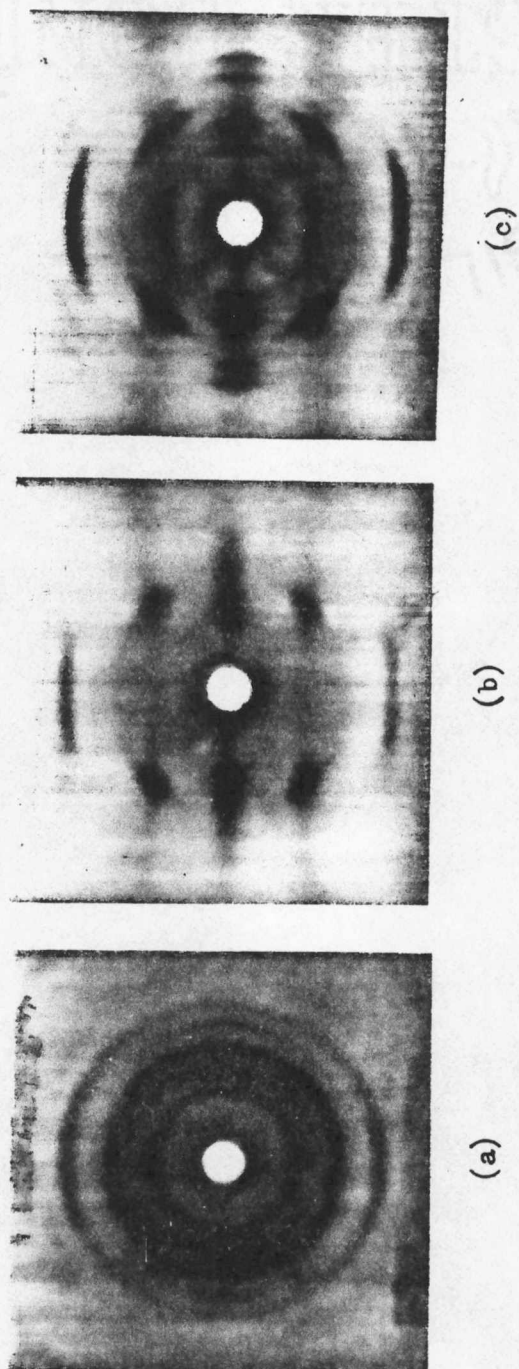


Figure IV.8. WAXS patterns of 6323, Take-up velocity 130m/min
(a) as-spun, (b) cold drawn 25°C, (c) hot drawn 150°C

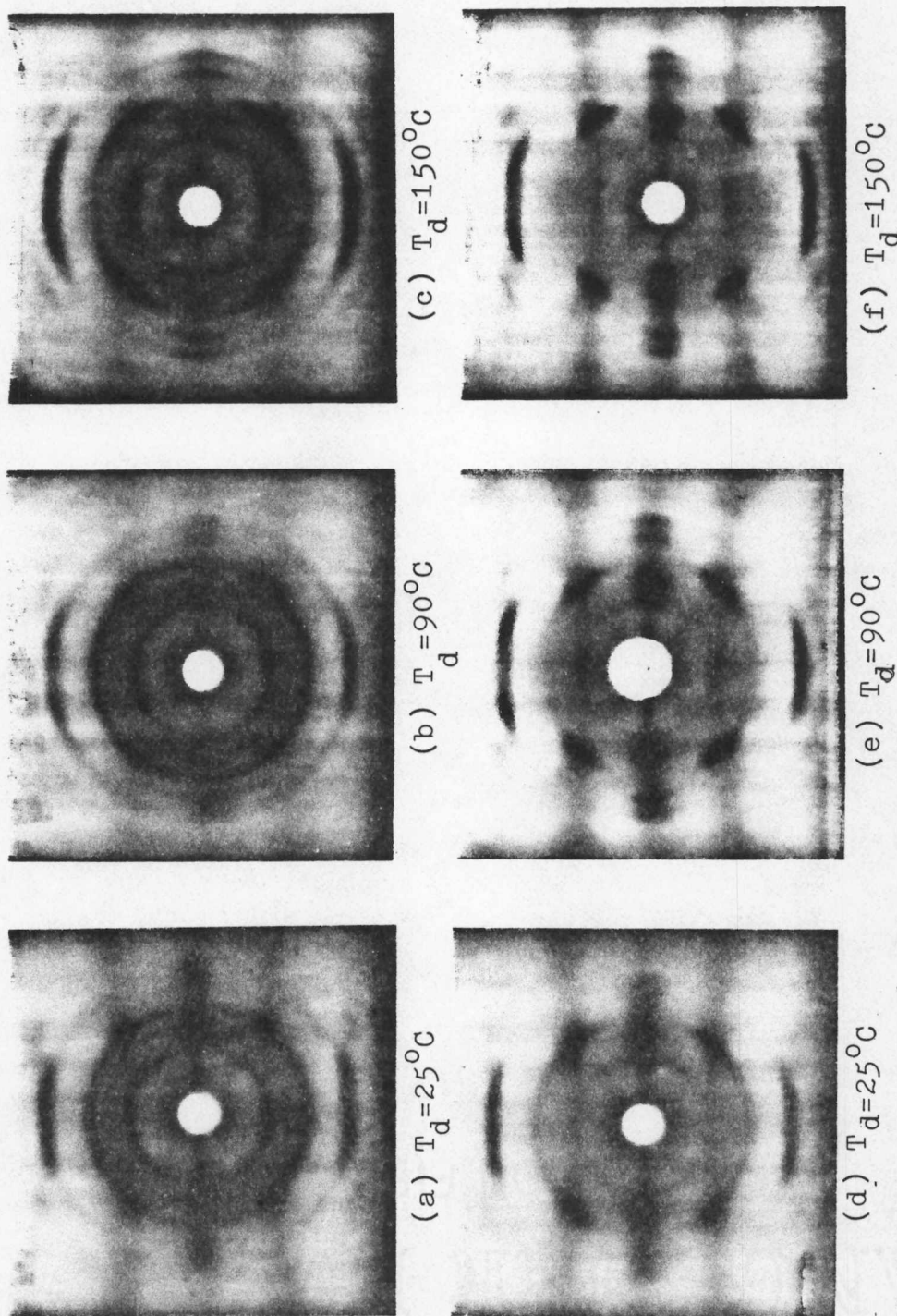


Figure IV.9. WAXS patterns for various molecular weight samples, take-up velocity 30 m/min, DR=6X
 (a,b,c) 5831-1-6-7
 (d,e,f) 6423

The quantitative orientation of the drawn filaments will be presented in the next two sections.

Birefringence

Table VIII give birefringence values for drawn samples. From this table, it can be seen that the values of birefringence increase with increasing draw ratio. Samuels (90) and Nadella et al (65) carried out detailed study of structure development in drawn polypropylene films and fiber. In their studies of drawing and annealing of polypropylene fibers they reported numerically similar values of birefringence for the drawn filaments. In addition higher molecular weight polymers in any given draw ratio seems to have higher birefringence.

Figure IV.10 presents a plot of birefringence of drawn fibers plotted versus draw temperature. It appears that there is little change in birefringence in the temperature range of 25-120°C. Above 120°C the birefringence decreases sharply with increasing draw temperature.

Orientation Factors

The crystalline orientation functions of drawn fibers were determined from the procedure described in Chapter III. Figure IV.11 shows Herman-Stein c-axis crystalline

TABLE VIII. BIREFRINGENCE FOR DRAWN FIBERS

POLYMER	TAKE-UP m/min	D.R. (X)	T (°C)	t (mm)	Δn (m μ)
6323	30	3.5	60	0.1666	31.2×10^{-3}
6323	30	3.5	90	0.1740	28.1×10^{-3}
6323	30	3.5	120	0.1598	31.1×10^{-3}
6323	30	3.5	150	0.1102	$20. \times 10^{-3}$
6323	30	6	60	0.155	33.4×10^{-3}
6323	30	6	90	0.1380	30.4×10^{-3}
6323	30	6	120	0.1524	34×10^{-3}
6323	30	6	150	0.1305	21.5×10^{-3}
6323	130	3.5	25	0.0795	31×10^{-3}
6323	130	3.5	60	0.0791	27.5×10^{-3}
6323	130	3.5	90	0.0700	25.5×10^{-3}
6323	130	3.5	150	0.0710	25×10^{-3}
6323	130	6	25	0.0584	33.3×10^{-3}
6323	130	6	60	0.0654	28.25×10^{-3}
6323	130	6	90	0.0720	30.7×10^{-3}
6323	130	6	150	0.0650	24.3×10^{-3}
6423	30	3.5	60	0.1521	32.5×10^{-3}
6423	30	3.5	90	0.1666	30×10^{-3}
6423	30	3.5	120	0.1521	29×10^{-3}
6423	30	3.5	150	0.1739	24.3×10^{-3}
6423	30	6	60	0.1304	35×10^{-3}

TABLE VIII. (continued)

POLYMER	TAKE-UP m/min	D.R. (x)	T. (°C)	t (mm)	Δn (m μ)
6423	30	6	90	0.1302	31.4×10^{-3}
6423	30	6	120	0.1312	35×10^{-3}
6423	30	6	150	0.166	30×10^{-3}
6423	130	3.5	25	0.081	33.1×10^{-3}
6423	130	3.5	60	0.0867	27.5×10^{-3}
6423	130	3.5	90	0.0942	31.2×10^{-3}
6423	130	3.5	150	0.0940	25.2×10^{-3}
6423	130	6	25	0.0800	35×10^{-3}
6423	130	6	60	0.0724	34×10^{-3}
6423	130	6	90	0.0867	31.2×10^{-3}
6423	130	6	150	0.0850	20×10^{-3}
106-7	30	3.5	25	0.0798	31.0×10^{-3}
106-7	30	3.5	60	0.1376	30.5×10^{-3}
106-7	30	3.5	90	0.1084	30×10^{-3}
106-7	30	3.5	150	0.1451	22×10^{-3}
106-7	30	6	25	0.1018	33×10^{-3}
106-7	30	6	60	0.1000	31.4×10^{-3}
106-7	30	6	90	0.1239	29.4×10^{-3}
106-7	30	6	150	0.1014	20×10^{-3}
106-7	130	3.5	25	0.0655	34.9×10^{-3}
106-7	130	3.5	60	0.0726	31.9×10^{-3}
106-7	130	3.5	90	0.0865	29.8×10^{-3}
106-7	130	3.5	150	0.0885	27.6×10^{-3}
106-7	130	6	25	0.0580	35×10^{-3}
106-7	130	6	60	0.0585	32×10^{-3}
106-7	130	6	90	0.0653	33×10^{-3}
106-7	130	6	150	0.0586	23×10^{-3}

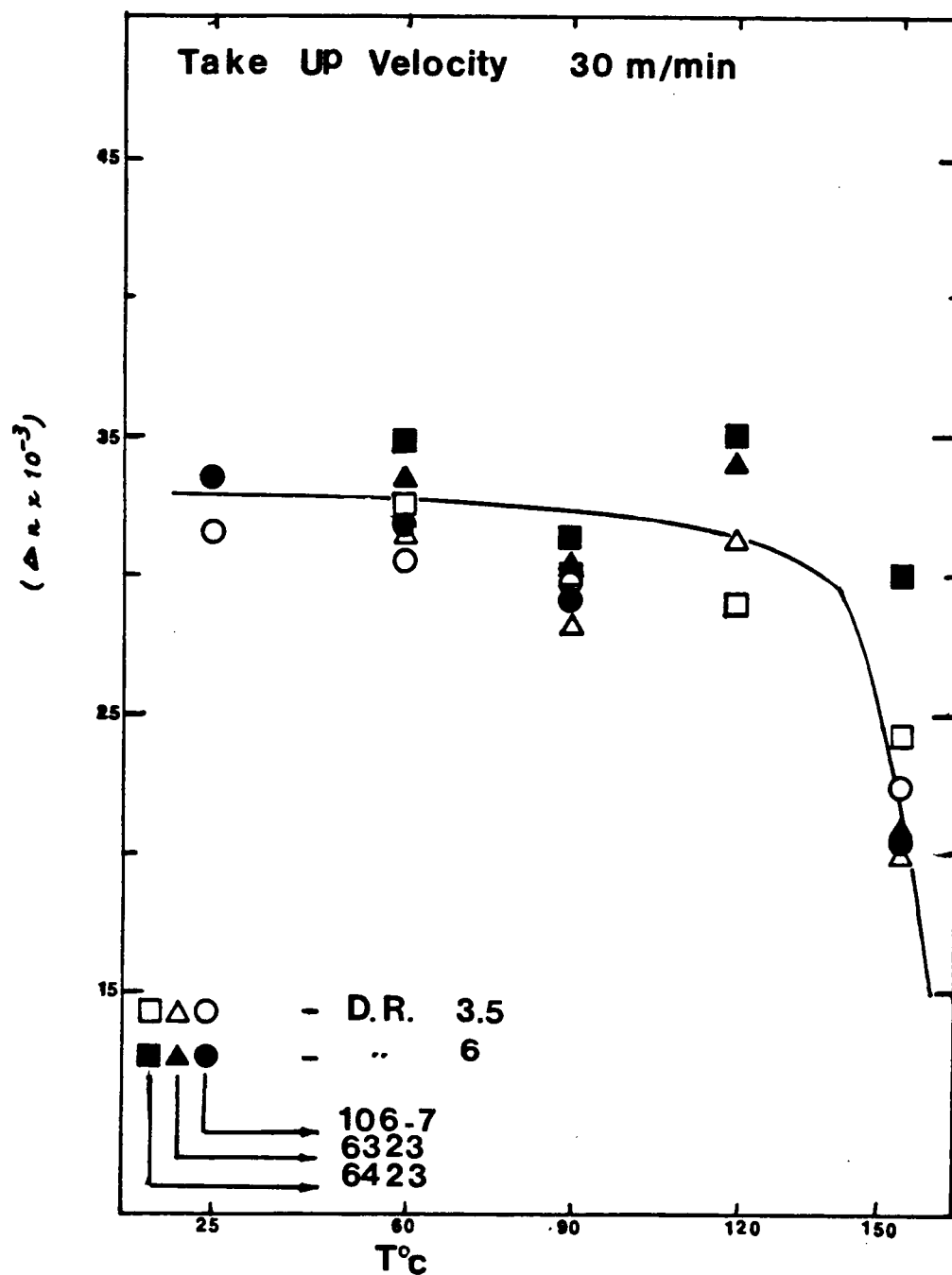


Figure IV.10. Birefringence vs draw temperature for drawn polypropylene fibers.

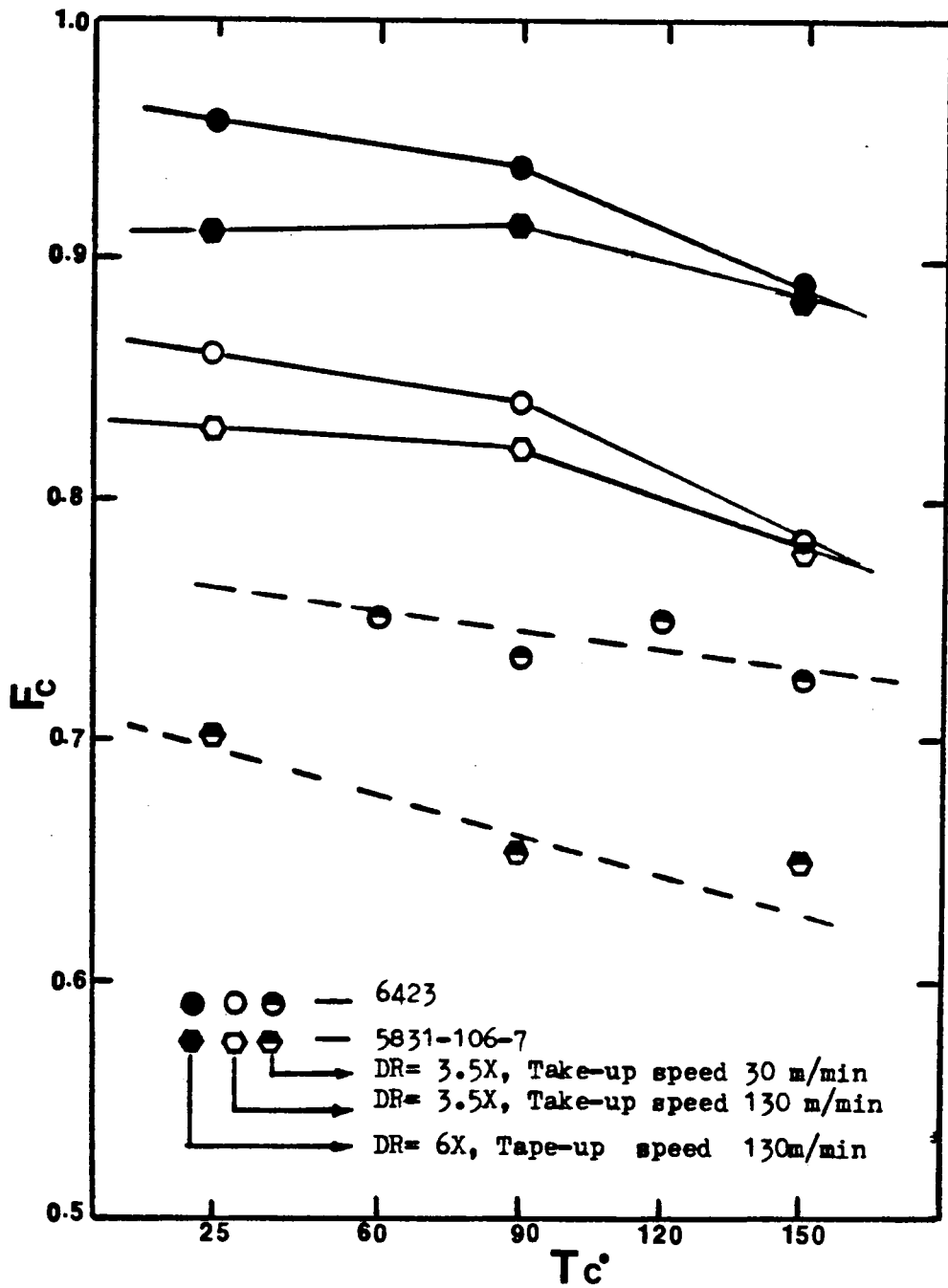


Figure IV.11. C-axis crystalline orientation function versus draw temperature for various drawn polypropylene fibers.

orientation function (f_c) for the drawn filaments plotted versus draw temperature. This Figure clearly indicates the effect of draw ratio, temperature, molecular weight, and spinline take-up velocity on the c-axis orientation factor (f_c). The samples which were initially more oriented (as melt spun) show larger c-axis orientation function values for any given draw ratio. At any given draw ratio f_c is also found to be higher for higher molecular weight samples.

There is a significantly higher value of f_c for samples with draw ratio of 6X than the samples with lower draw ratio (DR=3.5) for all three polymers. The general trend observed in this study was that both the birefringence and c-axis orientation factor f_c were observed to decrease with increasing draw temperature. The effect was largest in the higher temperature range above 120°C.

The values of f_c for all drawn filaments were found to lie in the range 0.65 to 0.95 which correlates well with the values obtained by Samuels (90) and Nadella et al (65).

Figure IV.12 shows the amorphous orientation function plotted versus draw temperature. The values of f_{am} for drawn fibers were in lower range (0.31 to 0.455) compared to the values of f_c . The behavior of amorphous orientation function with regard to draw temperature, draw ratio, molecular weight, and take-up speed during melt spinning was similar to the results obtained for c-axis crystalline orientation function (f_c).

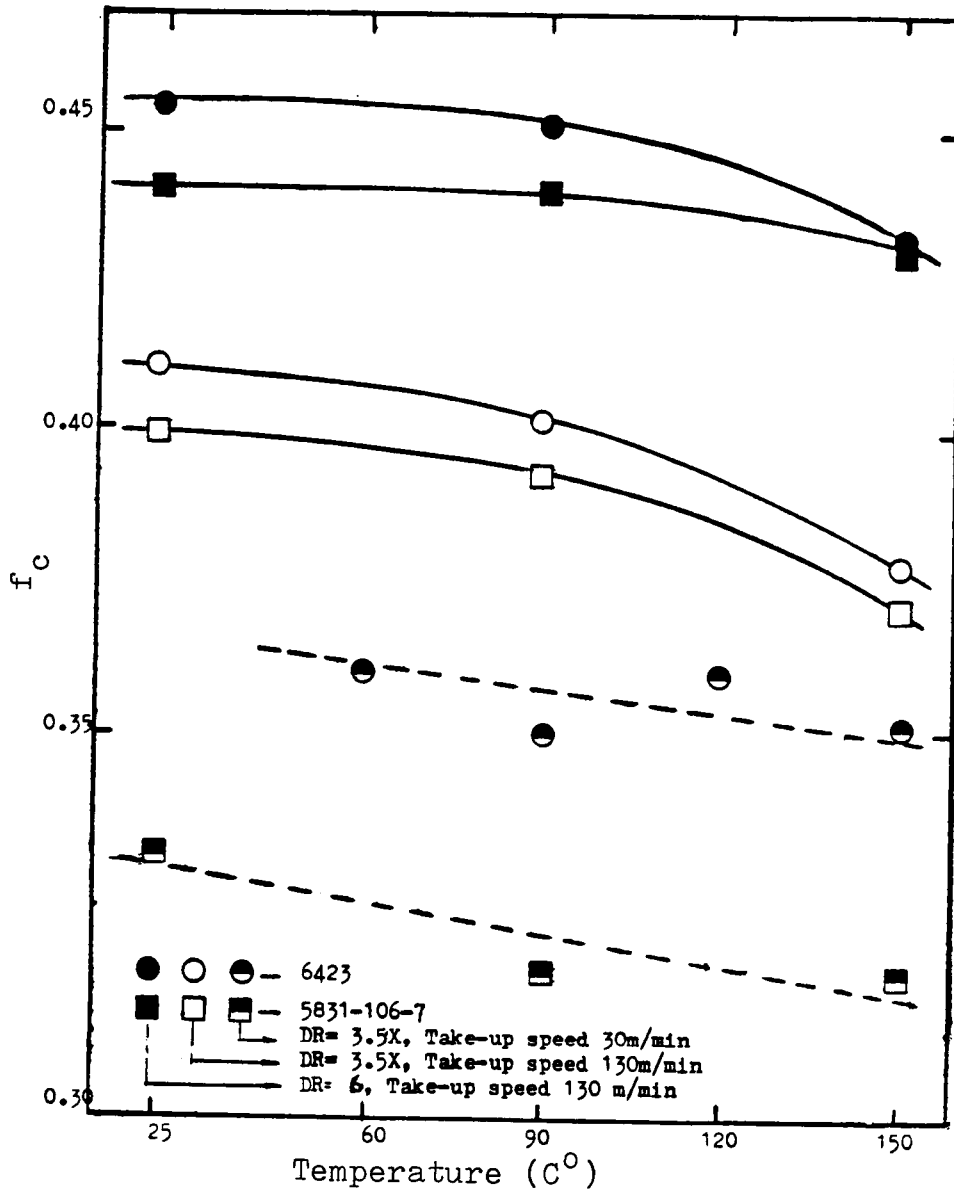


Figure IV.12. Amorphous orientation function (f_{am}) versus draw temperature for various drawn polypropylene fibers.

D. OBSERVATION OF FIBRILLATION

Scanning Electron Microscopy (SEM)

The scanning electron micrographs of the "peeled" drawn filaments were taken to investigate the internal structure of the filaments, as well as level of fibrillation.

The microstructure, as determined by SEM, will be compared with the data obtained by small angle x-ray diffraction and density measurements in the later sections of this chapter.

S.E.M. photomicrographs of selected polypropylene (6423) which were forceably split (peeled) after nicking with a razor blade, exhibited effects of drawing temperature on the level of fibrillation as shown in Figure IV.13. It is apparent from Figure IV.13 that there is a significant fibrillation evident at the drawing temperature of 25°C and as draw temperature increases the fibrillation decreases Figure IV.13,2-3-4.

The effect of draw ratio can be seen from the comparison of Figure IV.13 with Figure IV.14. It is clear that higher draw ratio samples show higher fibrillation at any given draw temperature. A careful observation of the fibrils indicates that for both draw ratios of 3.5X and 6X they are not uniformly circular in cross sections. This indication is not clearly dependent on sample preparation conditions or

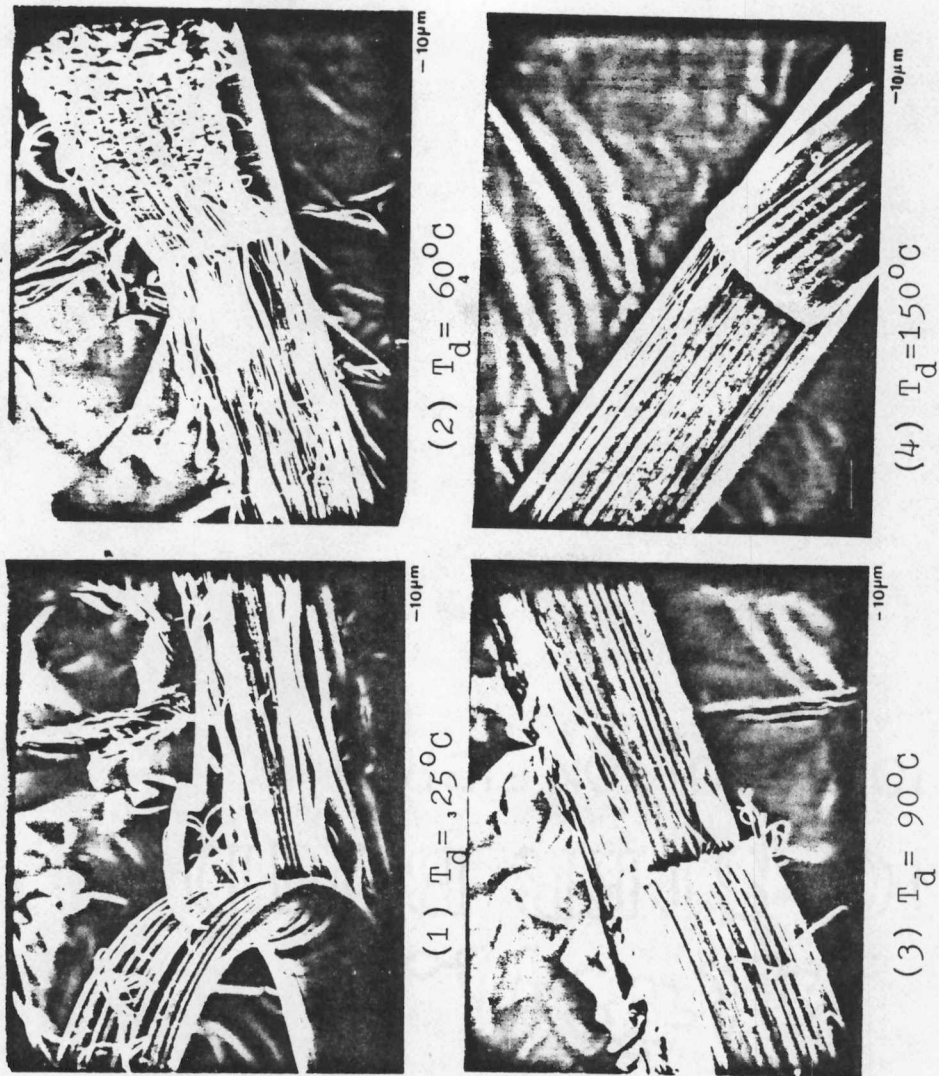


Figure IV.13. SEM photomicrographs of drawn polypropylene 6423 (take-up velocity 130m/min, DR=6X).

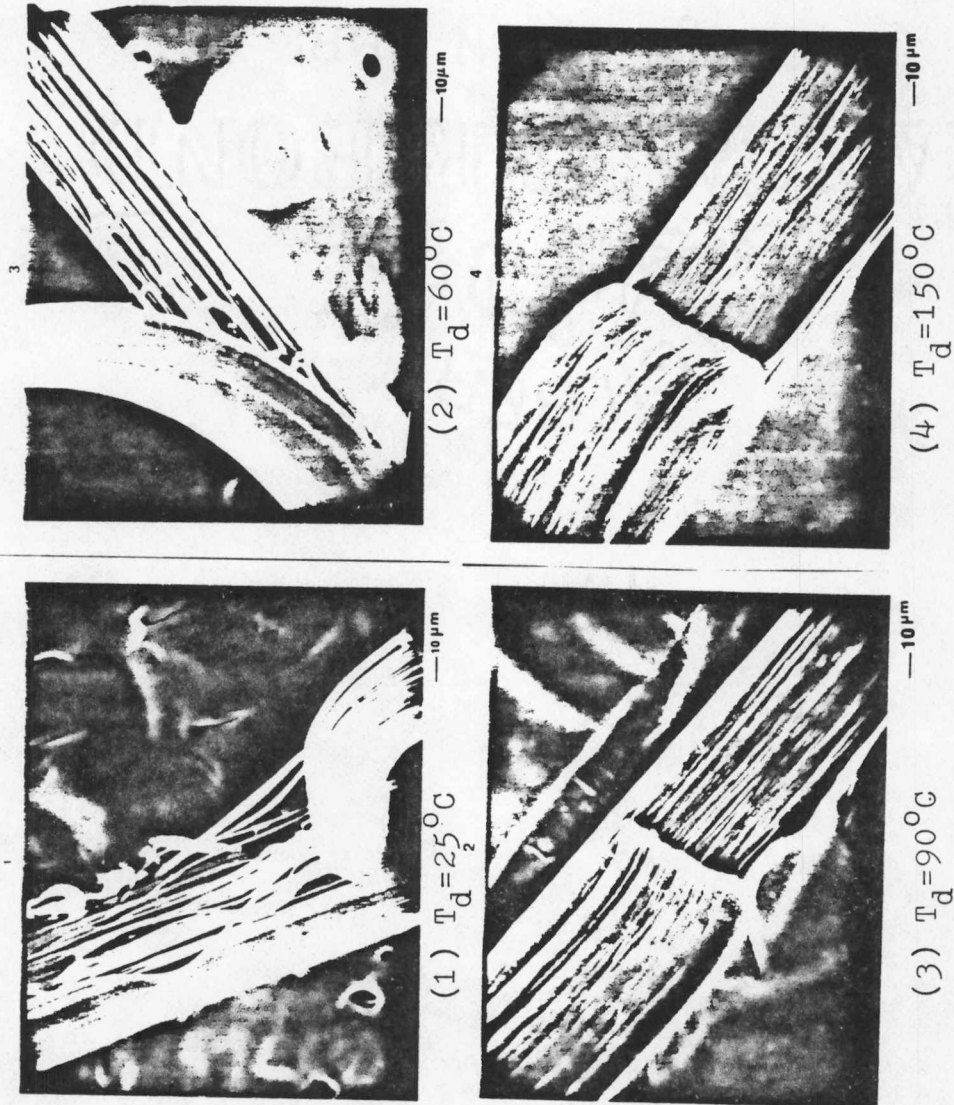


Figure IV.14. SEM photomicrographs of drawn polypropylene 6423 (take-up speed 130m/min, DR=3.5X)

mechanism of peeling. From a general point of view it seems that the filaments were drawn at 25°C are more or less ribbon like and the tendency toward splitting into smaller fibrils increase with draw temperature (below 100) Figure IV.13.

Figure IV.15. and Figure IV.16 exhibit respectively the effect of take-up velocity and weight average molecular weight on fibrillation for various drawn filaments. It can be seen from SEM photmicrographs of Figure IV.15 that at given draw ratio the amount of fibrillation increases with increasing take-up velocity during spinning. A similar tendency was observed where various molecular weight samples were compared as a function of draw ratio and draw temperature Figure IV. 16. In each case the higher molecular weight sample fibrillate more.

Density

The density of the polypropylene fibers were measured from density gradient column and subjected to calculation of crystallinity by a procedure mentioned in Chapter III. Since the computed crystallinity from density measurements is depend on microvoids within the fibers, these results were called the "apparent crystallinity".

The volume fraction of microvoids were estimated from the difference between the apparent crystallinity (density measurements) and crystallinity as determined from

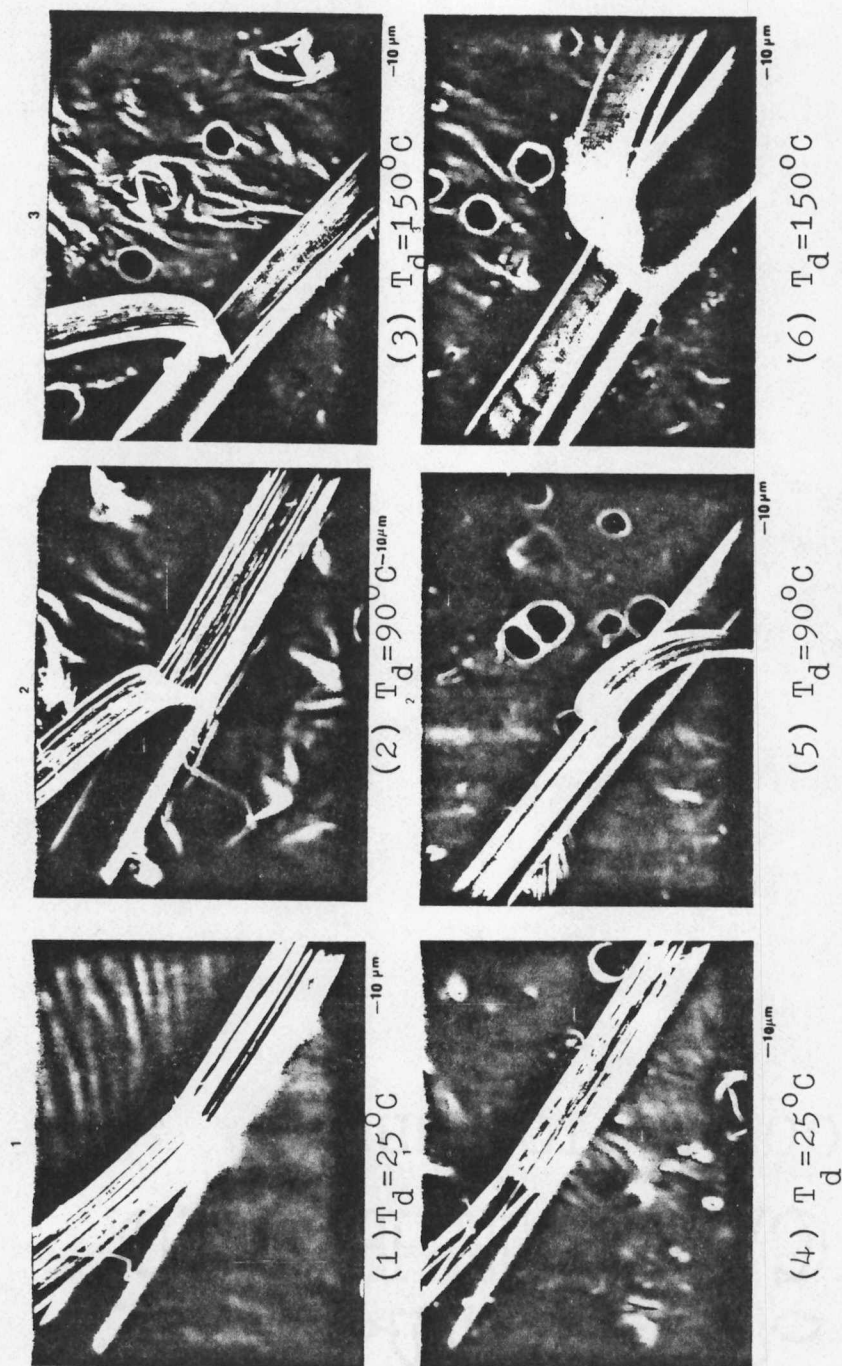


Figure IV.15. SEM photomicrographs of drawn polypropylene 5831-106-7 (DR=3.5X)
 (1,2,3) Take-up speed 130m/min
 (4,5,6) Take-up speed 30m/min

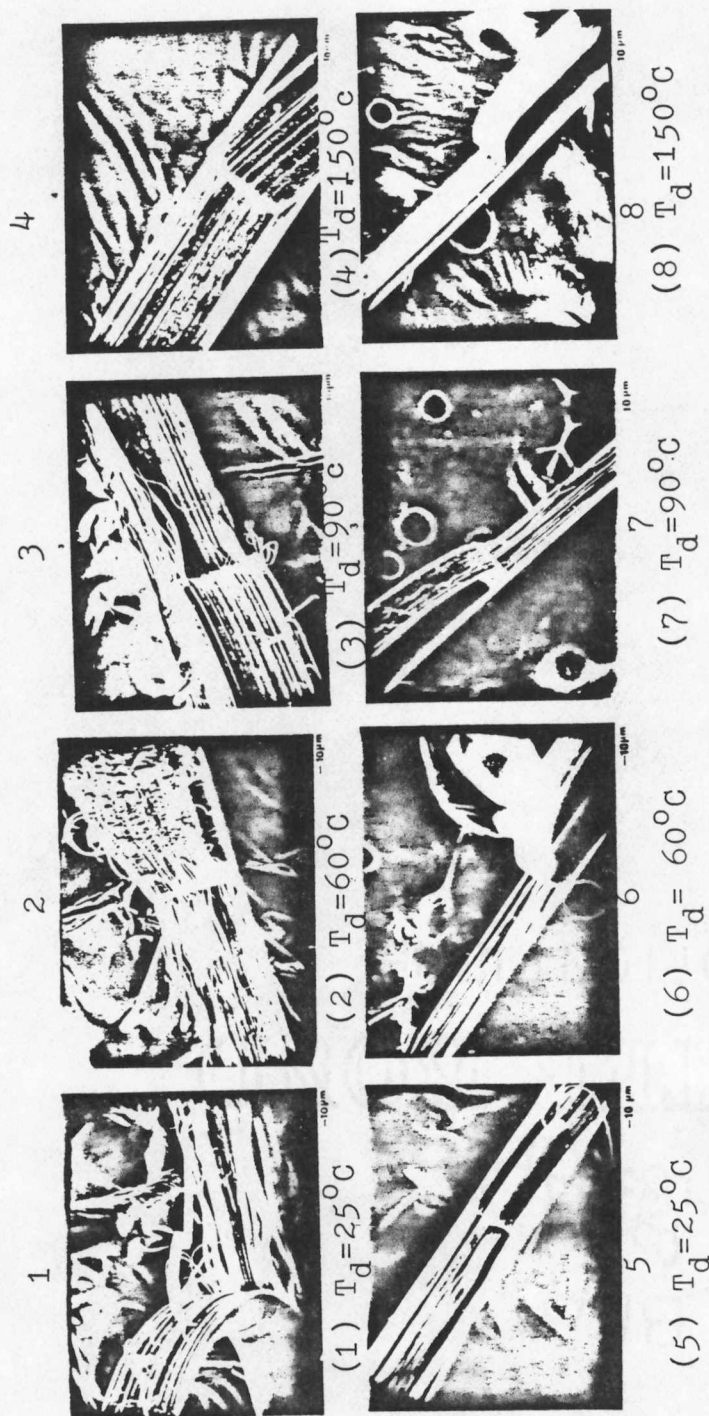


Figure IV.16. SEM photomicrographs for various molecular weight polypropylene fibers. (DR=6X, Take-up velocity 130m/min).

(1,2,3,4) 6423

(5,6,7,8) 5831-106-7

differential scanning calorimetry techniques.

Figure IV.17 indicates the changes in density and apparent crystallinity with respect to the draw ratio of the drawn fibers as a function of draw temperature. The density was found to decrease with increasing draw ratio until about 120°C and to be nearly independent of draw ratio. This change of density and apparent crystallinity at the higher draw temperature (150°C) was coupled with the observation of SEM patterns Figure IV.13, IV.14. The filaments were slightly fibrillated. It is also made clear from Figure IV.17 that the density increases gradually as draw temperature increases. This increase in density as a function of draw temperature together with a decrease of intensity, by increasing draw ratio, lead to the greater opening of the microvoids within the filaments drawn at lower temperature and higher draw ratio.

Apparent crystallinity was plotted versus draw temperature in Figure IV.18 for all three various molecular weight polypropylene drawn under various conditions. From this figure it is apparent that the fibers spun at higher take-up velocity which had higher molecular orientation before drawing are revealed to also have lower density or apparent crystallinity at any given draw ratio. It was found that the higher molecular weight samples also exhibit lower density than lower molecular weight samples in any given draw condition.

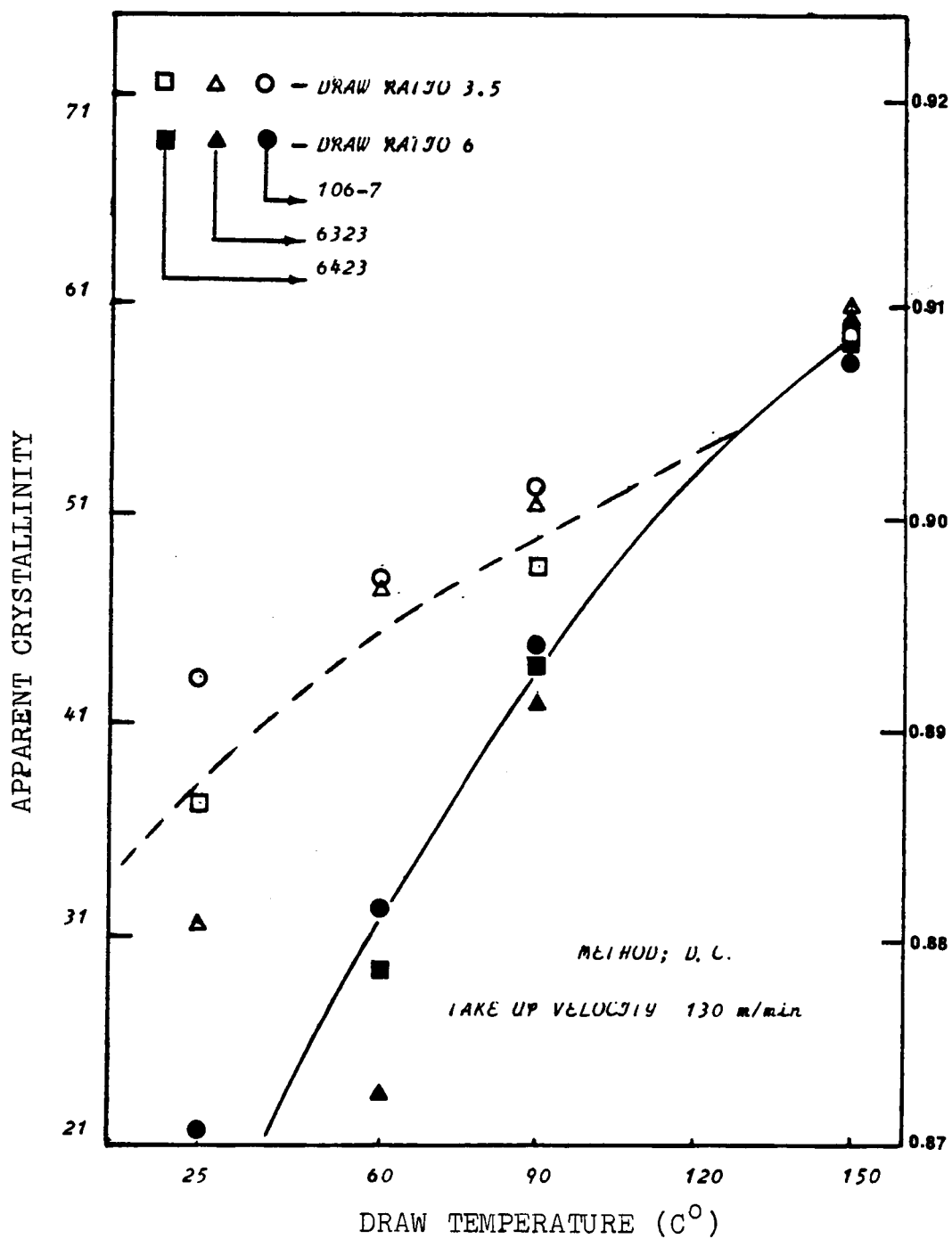


Figure IV.17. Apparent crystallinity vs draw temperature (take-up velocity 130m/min)

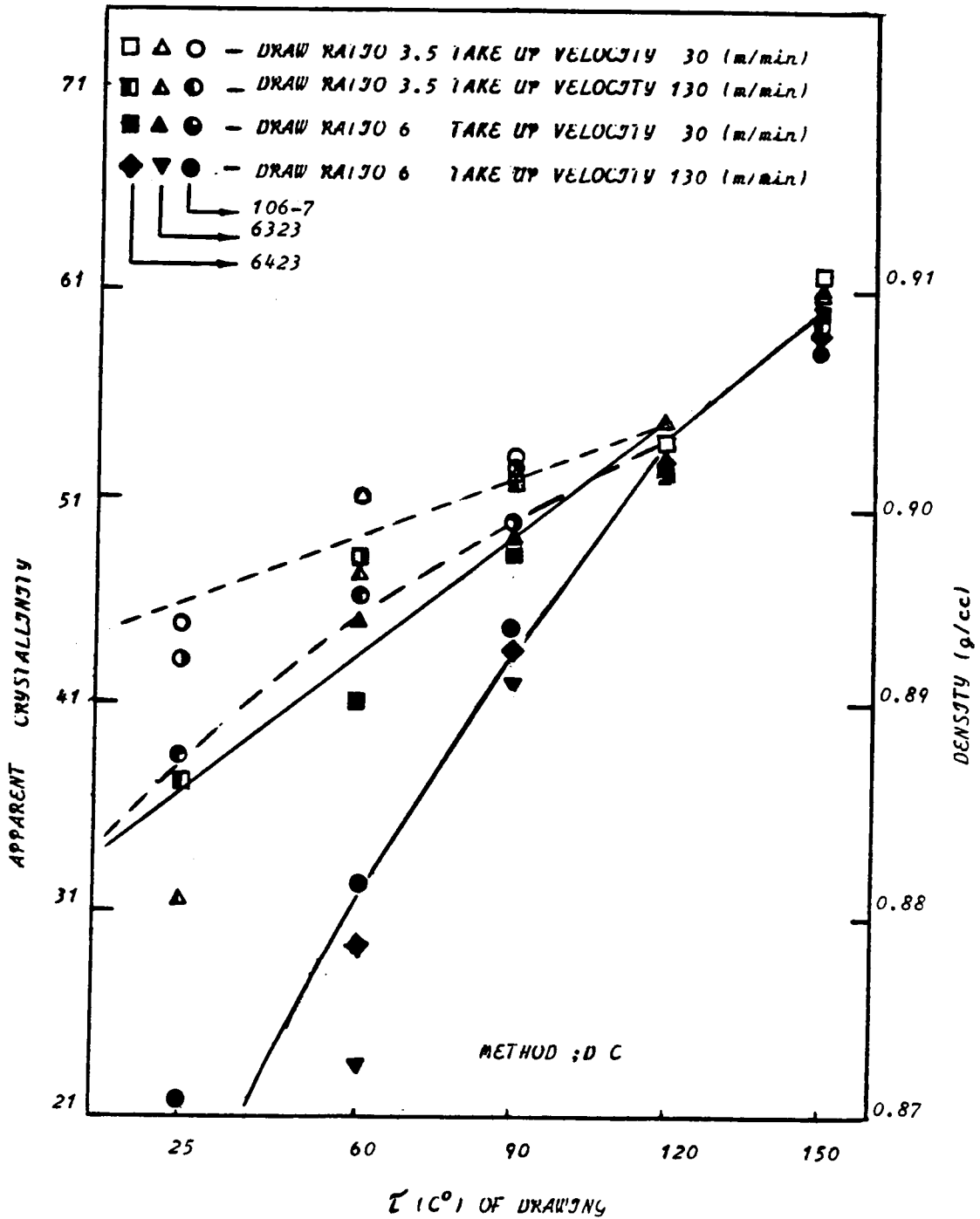


Figure IV.18. Density and apparent crystallinity vs temperature of drawing of polypropylene fibers.

Figure IV.19 represents a plot of both the percent crystallinity computed from DSC technique and percent crystallinity (density), from density gradient column versus draw temperature. From this figure a logical conclusion is that since crystallinity measurements from DSC technique are free of any effect due to voids the differences among the two curves represent the amount of void as a function of draw temperature. Since increasing fibrillation should increase the void fraction these results are definitely supportive of the results obtained by scanning electron microscope.

The volume fraction of microvoids were estimated from a combination of these two techniques, will be compared and correlated with microvoid fractions computed from the quantitative SAXS measurements in the later section of this chapter.

Qualitative Small Angle X-ray Scattering (SAXS)

Figure IV.20 contains SAXS patterns of polypropylene specimens drawn with two draw ratios (3.5X,6X) at 25^o, 90^o and 150^oC. The patterns for the filaments drawn at 25^oC, show a major reduction of the intensity of the meridional scattering compared to the melt-spun filaments and very intense diffuse equatorial scattering. The origin of this diffuse equatorial scattering would seem to be the presence of voids (74,3,65) elongated in the direction of the fiber

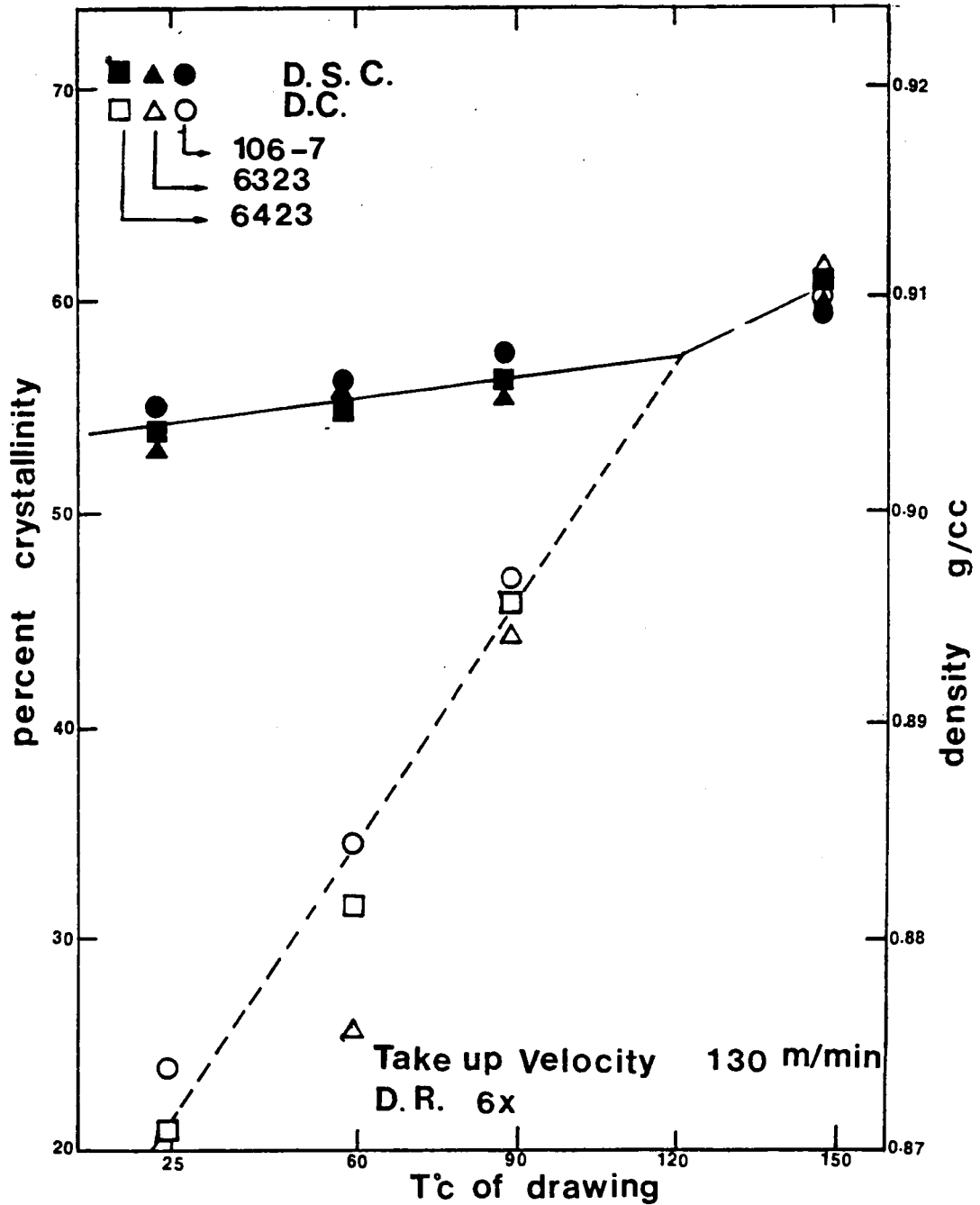


Figure IV.19. Percent crystallinity and apparent crystallinity as a function of draw temperature.

axis. The patterns of Figure IV.20-a and IV.20-d show a diminutive degree of discrete scattering which appears to be associated with a long period in the filaments. It is apparent that the diffuse equatorial scattering for the filaments drawn at 25°C increase with draw ratio and that the discrete scattering becomes insignificant as the draw ratio increases. The absence of discrete meridional scattering is associated with an absence of segregated chain-folded chains. It is impossible to distinguish between the extended chain structure and the integrated chain-fold structure by qualitative SAXS patterns, since both of the structure are consistent with the scattering pattern.

Effects of draw temperature on void formation is apparent from Figure IV.20. The patterns for the filaments drawn at 90°C and 150°C show reduced diffuse equatorial scattering and the development of a two-point pattern on the meridian corresponding to the long period spacing. The two-point pattern on the meridional scattering becomes more intense and diffuse equatorial scattering decreases with increasing draw temperature. The long period dimensions varied from about 120 Å to about 210 Å. The SAXS patterns of the hot drawn fibers (150°C) showed somewhat larger dimensions (190 Å to 210 Å).

Figure IV.21 shows the comparison of SAXS patterns for 6423 (melt index 6.6) and 5831-106-7 (melt index 25). It can be seen from SAXS patterns in this figure that the higher

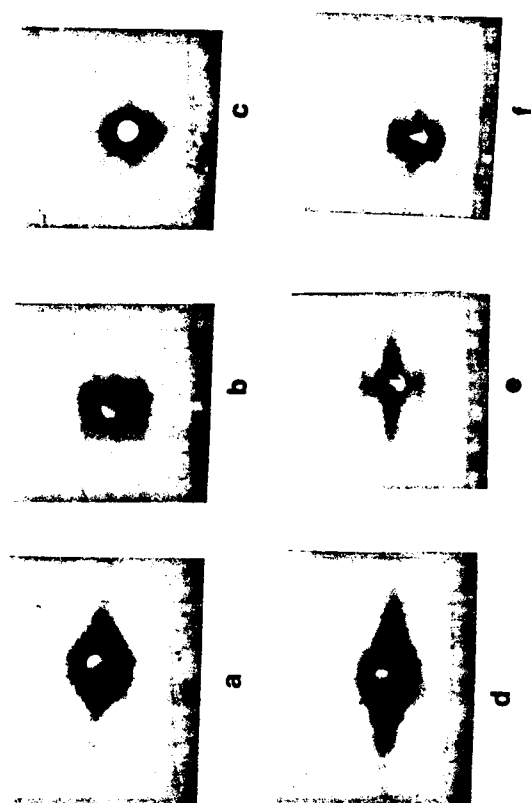


Figure IV.20. SAXS patterns of drawn 6323 with take-up velocity 130m/min. (a) D.R.=3.5, $T_d=25^\circ\text{C}$, (b) D.R.=3.5, $T_d=90^\circ\text{C}$, (c) D.R.=3.5, $T_d=150^\circ\text{C}$, (d) D.R.=6, $T_d=25^\circ\text{C}$, (e) D.R.=6, $T_d=90^\circ\text{C}$, (f) D.R.=6, $T_d=150^\circ\text{C}$

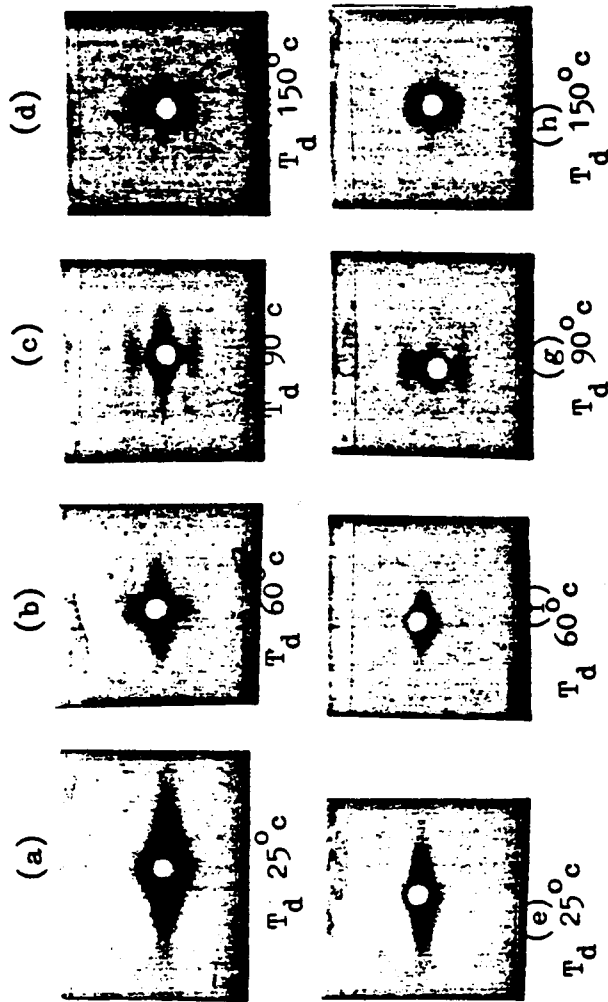


Figure IV.21. SAXS patterns of polypropylene fibers with DR=6X, take-up velocity 130m/min
 (a-d) 6423
 (e-h) 5831-106-7

molecular weight samples contained more voids at cold draw temperature and there is a similar trend as a function of temperature with appropriate patterns in Figure IV.20.

The effects of take-up velocity (initial orientation in the spun filaments) on fibrillation or opening of the voids within the fibers are shown from SAXS patterns in Figure IV.22. The SAXS patterns of the samples with a higher initial orientation (as melt spun) exhibit a stronger diffuse equatorial scattering intensity for any given draw ratio indicating present of voids, which increase as take-up velocity increases.

Quantitative Small Angle X-ray Scattering (SAXS)

Based on preliminary qualitative measurements, selected specimens were quantitatively studied for further understanding of the interaction of processing variables on fibrillation and microvoid formation using the 10 meter small angle x-ray facility at the NCSASR, located in the Oak Ridge National Laboratory in Oak Ridge, Tennessee.

Figure IV.23 IV.24 IV.25 and IV.26 show example contour plots for drawn fibers as a function of draw temperature, draw ratio, molecular weight, and take-up velocity respectively. These plots show that the diffuse equatorial scattering which is caused by the presence of microvoids, increases with; 1) decrease in draw temperature, 2) increase

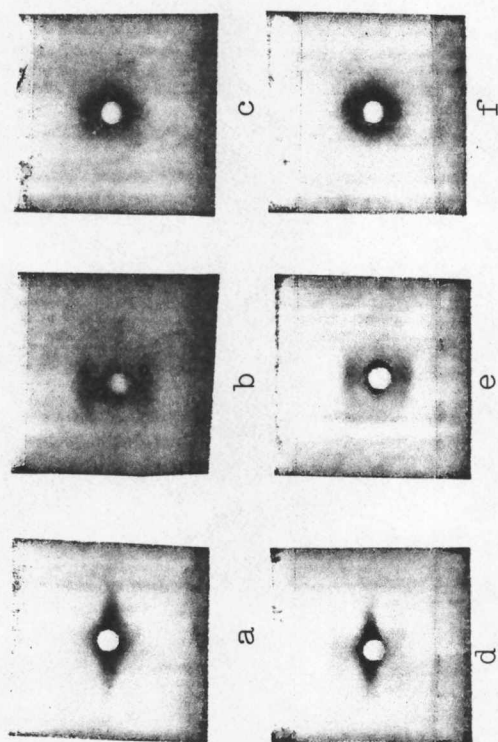


Figure IV.22. SAXS patterns of
polypropylene 5831-106-7, DR=3.5
(a-c) Take-up velocity 130m/min
(d-f) Take-up velocity 30m/min

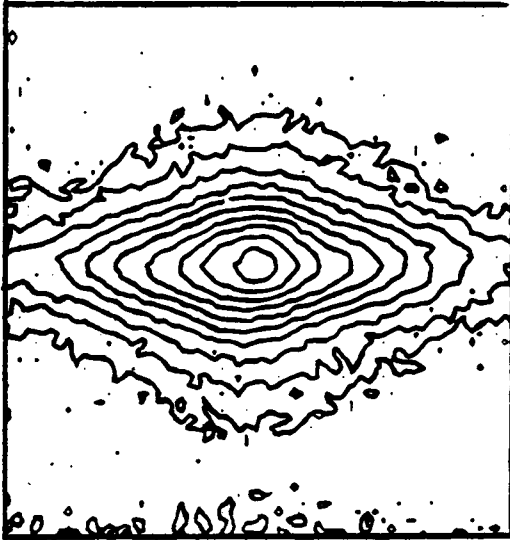
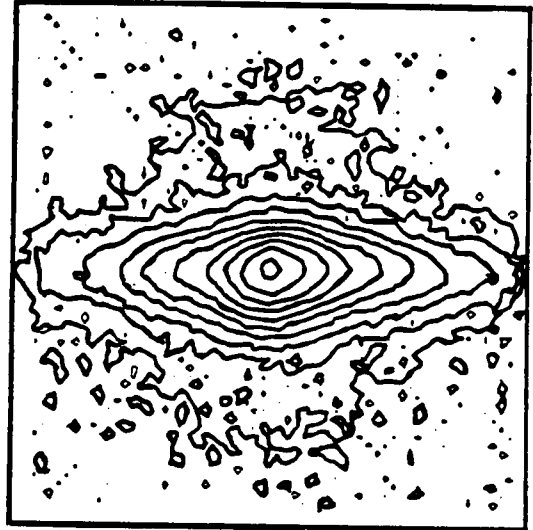
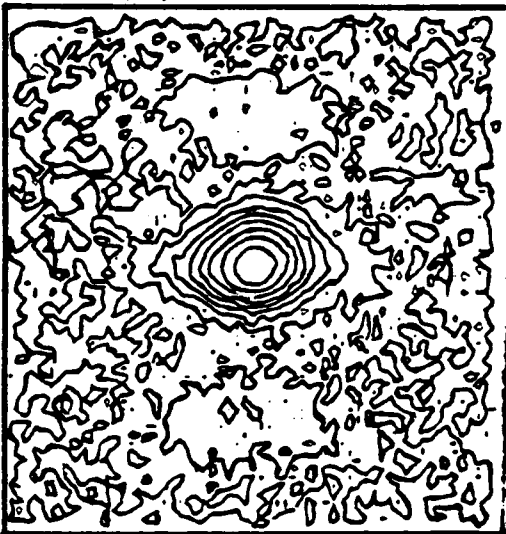
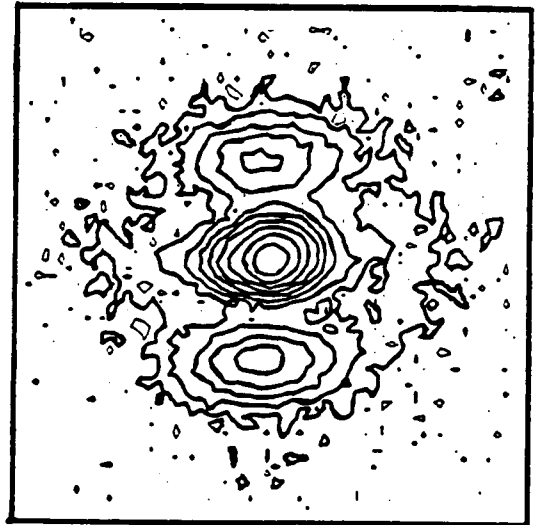
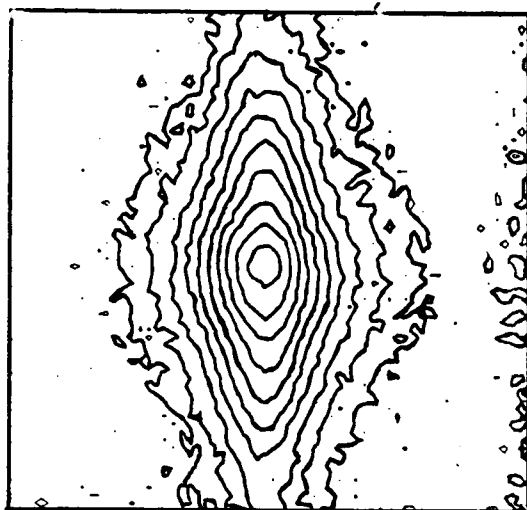
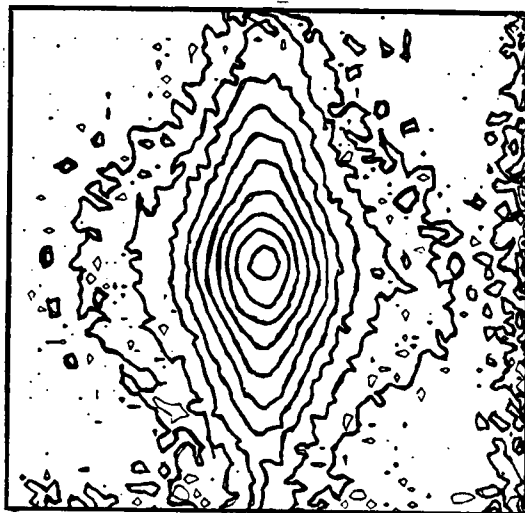
PP 6423**DR = 6****T 25****T 60****T 90****T 150**

Figure IV.23. SAXS contours plots for selected drawn fibers as a function of draw temperature

PP 6423 25 C°



DR 6

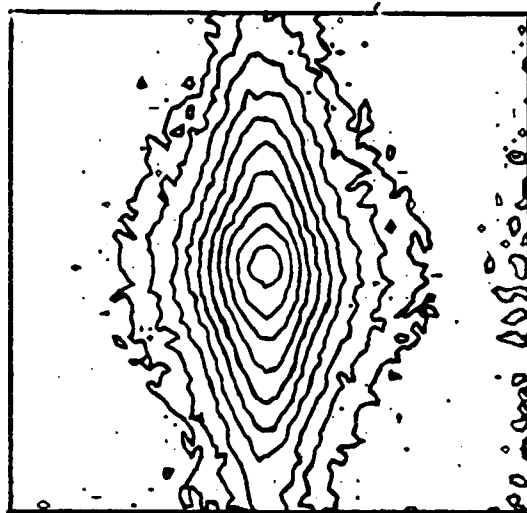


DR 3.5

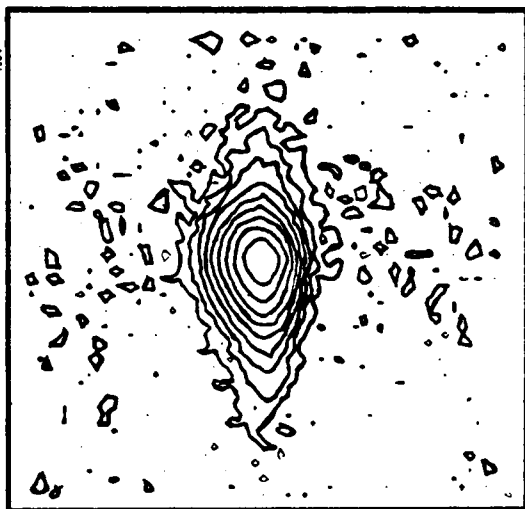
Figure IV.24. SAXS contour plots for selected drawn fibers as a function of draw ratio.

DR = 6

T 25c°



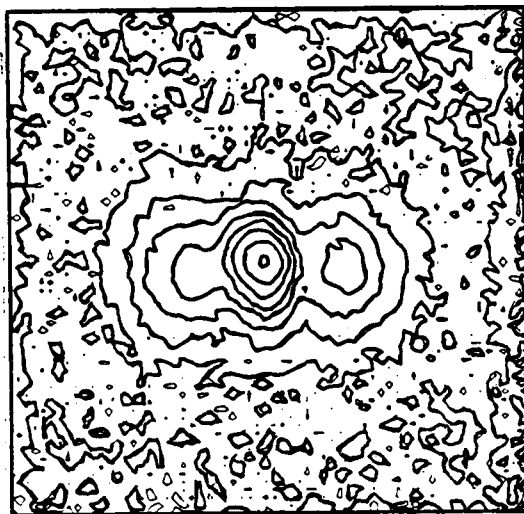
PP 6423



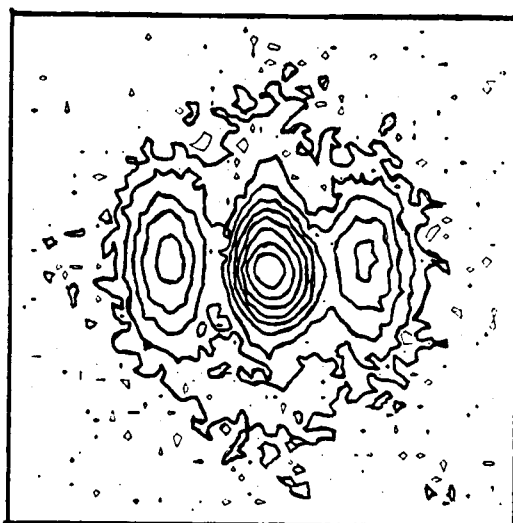
PP 106-7

Figure IV.25. SAXS contour plots for selected drawn fibers as a function of molecular weight of polypropylene.

PP 6423 DR · 6 T = 150



Take -Up 30 m/min



Take-Up 130 m/min

Figure IV.26. SAXS contour plots for selected drawn fibers as a function of take-up velocity during melt spinning

in draw ratio, 3) increase of molecular weight of the polypropylene, and 4) increase of take-up velocity in the as-spun filament in agreement with the qualitative results obtained from the film patterns.

Invariant Analysis. The volume fraction of microvoids was computed from the total integrated intensity scattered near the origin of reciprocal space. This integrated intensity is called the invariant, Q , of the scattered intensity and is given by,

$$Q = \int I(\bar{S}) dv_s \quad (24)$$

where $\bar{S}$ is the diffraction vector, dv_s is a volume element in reciprocal space. The integral is taken over the entire intensity distribution near the origin in reciprocal space.

For a cylindrically symmetric distribution of scattered intensity Q is given in terms of the intensities measured on the detector plane by,

$$Q_d = \frac{\pi \iint S_2 I(S_2, S_1) ds_2 ds_1}{I_0 (CT) (TM)} \quad (25)$$

and

$$Q = \frac{1}{(a \lambda)^3} Q_d \quad (26)$$

Here, S_2 is the horizontal coordinate on the detector plane (perpendicular to the fiber axis of the fiber samples), S_1 is the vertical coordinate on the detector plane (parallel to the fiber axis). $I(S_2, S_1)$ is the measured intensity at coordinates S_2, S_1 for some fixed counting time, CT , I_0 is

the intensity of the incident beam, and TM is the sample transmission factor. The latter quantity corrects the measurements for absorption in the sample. Also "a" is the specimen to detector distance and λ is the wavelength of radiation.

Following the arguments of Kratky and Miholic (58) it can be shown that the mean square fluctuation of the electron density is given by,

$$\overline{(\rho - \bar{\rho})^2} = K Q_d \quad (27)$$

$$\text{where, } K = 1 / (i_e N^2 d a \lambda^3) \quad (28)$$

Here i_e is the Thomson scattering constant for a free electron (7.9×10^{-26}), N is Avogadro's number, d is the specimen thickness in centimeters, a is the specimen to detector distance in centimeters, λ is the wavelength in centimeters. For a system of two uniform phases a general expression for mean square electron density fluctuation is given (3) as follows,

$$\overline{(\rho - \bar{\rho})^2} = (\rho - \rho_o)^2 W_1 W_o \quad (29)$$

with the assumption of $W_1 + W_o = 1$ where,

ρ_o = polymer electron density

ρ_1 = void electron density

W_o = volume fraction of polymer

W_1 = volume fraction of void

One can write equation into,

$$\overline{(\rho - \bar{\rho})^2} = \rho_o^2 W_1 (1 - W_1) \quad (30)$$

ρ_o is given by,

$$\rho_0 = d' / mZ \quad (6.02 \times 10^{23}) \quad (31)$$

d' = density

M = Molecular weight

Z = atomic number

The above expressions were used to measure the volume fraction of microvoids (Table IX) and to compare them with microvoid fractions estimated from a combination of crystallinity (DSC technique) and density measurements. This comparison is shown in Figure IV.27, IV.28, IV.29, as a function of draw temperature for various drawn polypropylene fibers. It can be concluded from these figures that the volume fraction of microvoids increase with 1) increase in draw ratio, 2) increase molecular weight, 3) decrease in temperature of drawing and 4) increase of take-up velocity during melt spinning of the fiber.

It is also clear from Figure IV.27, IV.28, IV.29, that there is good agreement between the void fractions measured by x-ray technique and those obtained from combination of density and DSC measurements. To further check this correlation a plot was made of the volume fraction of microvoids, measured from x-ray diffraction technique versus microvoid fraction measured by density. This is shown in Figure IV.30. The line draw is at 45° to the two coordinate axes and there is an excellent correlation. These results prove that the x-ray scattering is due to microvoids.

Table IX. VOID FRACTIONS FOR SELECTED DRAWN FIBERS MEASURED FROM INVARIANT ANALYSIS

POLYMER	TAKE-UP (%/in.)	D.R.(X)	T (C°)	Q	MSDF	W ₁
6423 (4378)	130	6	25	0.746x10 ⁻¹	0.549x10 ⁻²	0.28x10 ⁻¹
6423 (4381)	130	6	60	0.139x10 ⁻¹	0.102x10 ⁻²	0.52x10 ⁻²
6423 (4380)	130	6	90	0.222x10 ⁻²	0.164x10 ⁻³	0.89x10 ⁻³
6423 (4368)	130	6	150	0.222x10 ⁻²	0.165x10 ⁻³	0.83x10 ⁻³
6423 (4383)	130	3.5	25	0.195x10 ⁻¹	0.144x10 ⁻²	0.73x10 ⁻²
6423 (4398)	130	3.5	90	0.126x10 ⁻²	0.930x10 ⁻⁴	0.59x10 ⁻³
6423 (4382)	130	3.5	150	0.126x10 ⁻²	0.928x10 ⁻⁴	0.46x10 ⁻³
6423 (4394)	30	6	60	0.103x10 ⁻¹	0.757x10 ⁻³	0.38x10 ⁻²
6423 (4393)	30	6	150	0.172x10 ⁻¹	0.124x10 ⁻³	0.62x10 ⁻³
6423 (4396)	30	3.5	60	0.522x10 ⁻²	0.384x10 ⁻³	0.19x10 ⁻²
6423 (4397)	30	3.5	120	0.893x10 ⁻³	0.657x10 ⁻⁴	0.33x10 ⁻³
6423 (4395)	30	3.5	150	0.149x10 ⁻²	0.1098x10 ⁻³	0.25x10 ⁻³
6323 (4386)	130	6	25	0.593x10 ⁻¹	0.437x10 ⁻²	0.22x10 ⁻¹
6323 (4387)	130	6	150	0.188x10 ⁻²	0.139x10 ⁻³	0.70x10 ⁻³
5831-106-7 (4384)	130	6	25	0.460x10 ⁻²	0.339x10 ⁻²	0.17x10 ⁻²
106-7(4607)	130	6	90	0.170x10 ⁻²	0.125x10 ⁻³	0.83x10 ⁻³
106-7(4385)	130	6	150	0.210x10 ⁻²	0.155x10 ⁻³	0.78x10 ⁻³
106-7(4608)	130	3.5	150	0.174x10 ⁻²	0.128x10 ⁻³	0.64x10 ⁻³
106-7(4609)	130	3.5	25	0.100x10 ⁻¹	0.736x10 ⁻²	0.37x10 ⁻²
106-7(4613)	30	6	25	0.110x10 ⁻¹	0.155x10 ⁻²	0.78x10 ⁻³
106-7(4611)	30	6	90	0.114x10 ⁻²	0.837x10 ⁻⁴	0.42x10 ⁻³
106-7(4610)	30	6	150	0.135x10 ⁻²	0.889x10 ⁻⁴	0.60x10 ⁻³
106-7(4616)	30	3.5	25	0.317x10 ⁻²	0.234x10 ⁻³	0.12x10 ⁻³
106-7(4615)	30	3.5	90	0.838x10 ⁻³	0.617x10 ⁻⁴	0.31x10 ⁻³
106-7(4614)	30	3.5	150	0.128x10 ⁻²	0.942x10 ⁻⁴	0.48x10 ⁻³

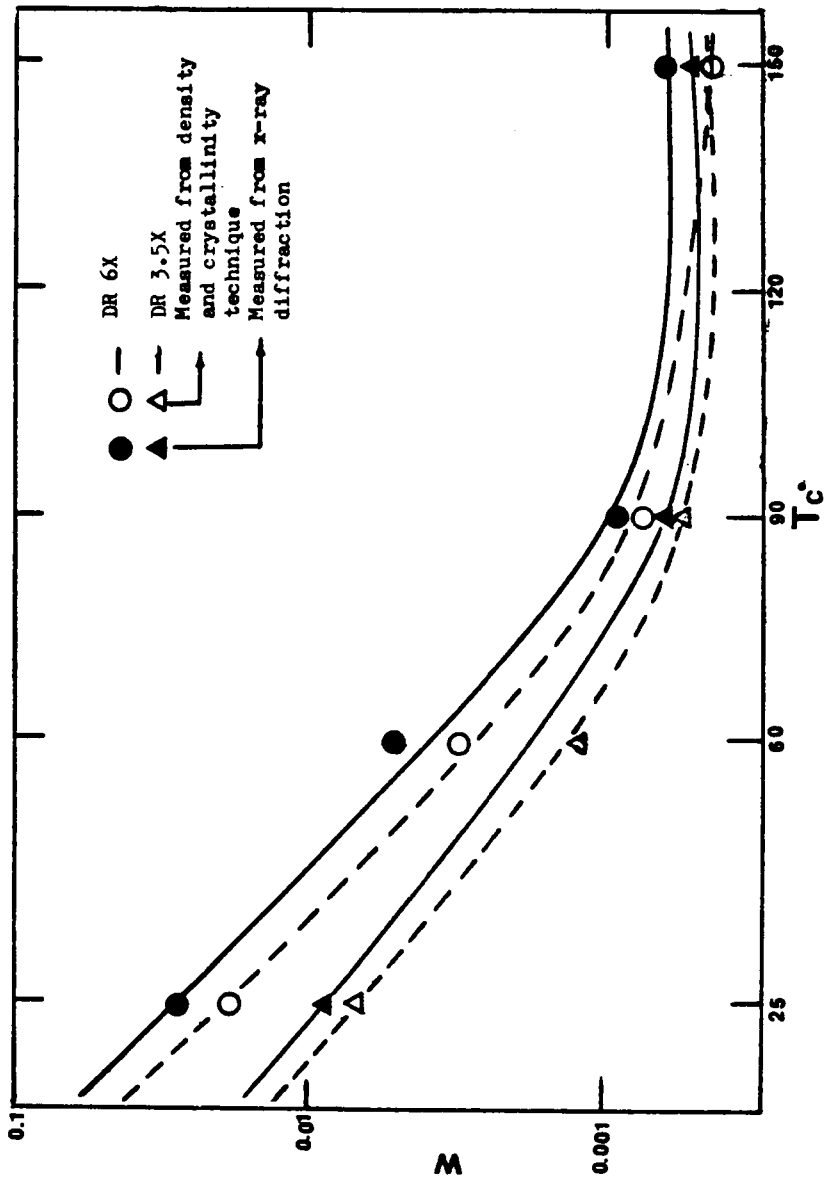


Figure IV.27. Void fraction as a function of draw temperature (effect of draw ratio).

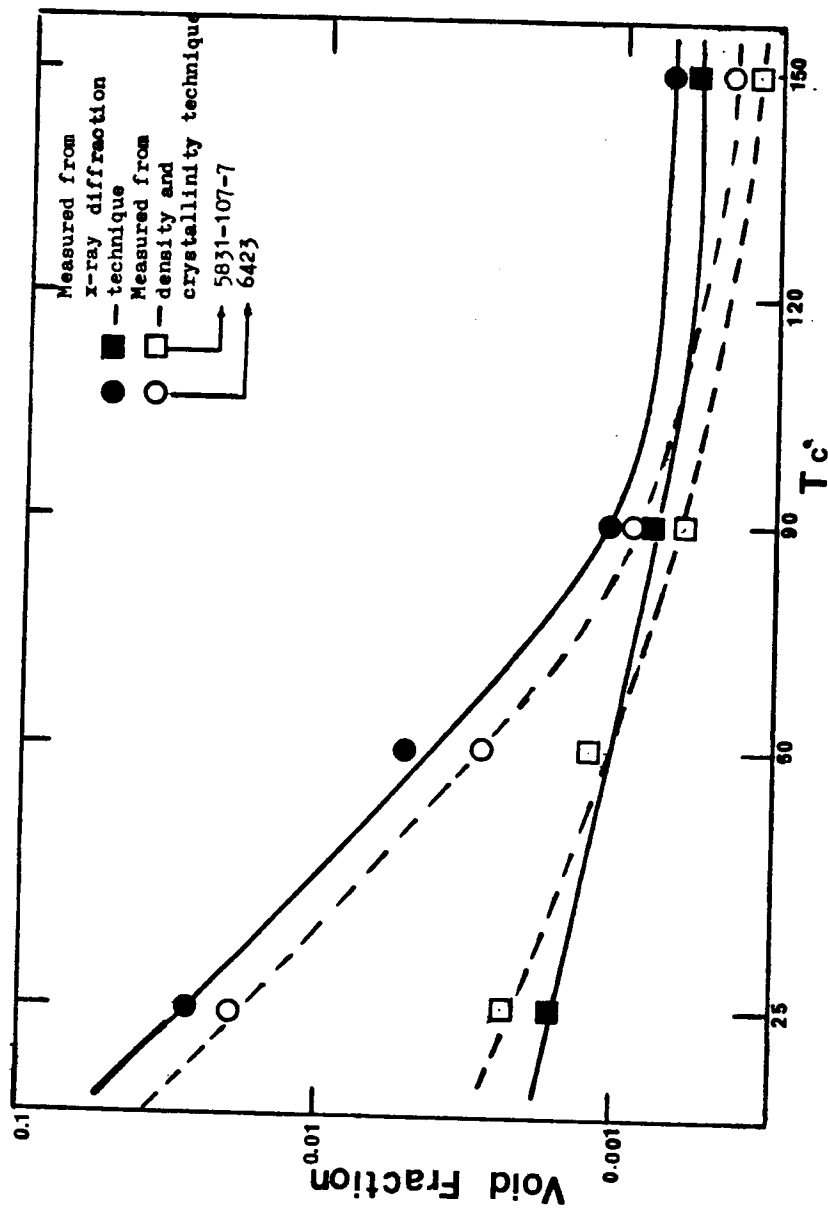


Figure IV.28. Void fraction as a function of draw temperature (effect of molecular weight).

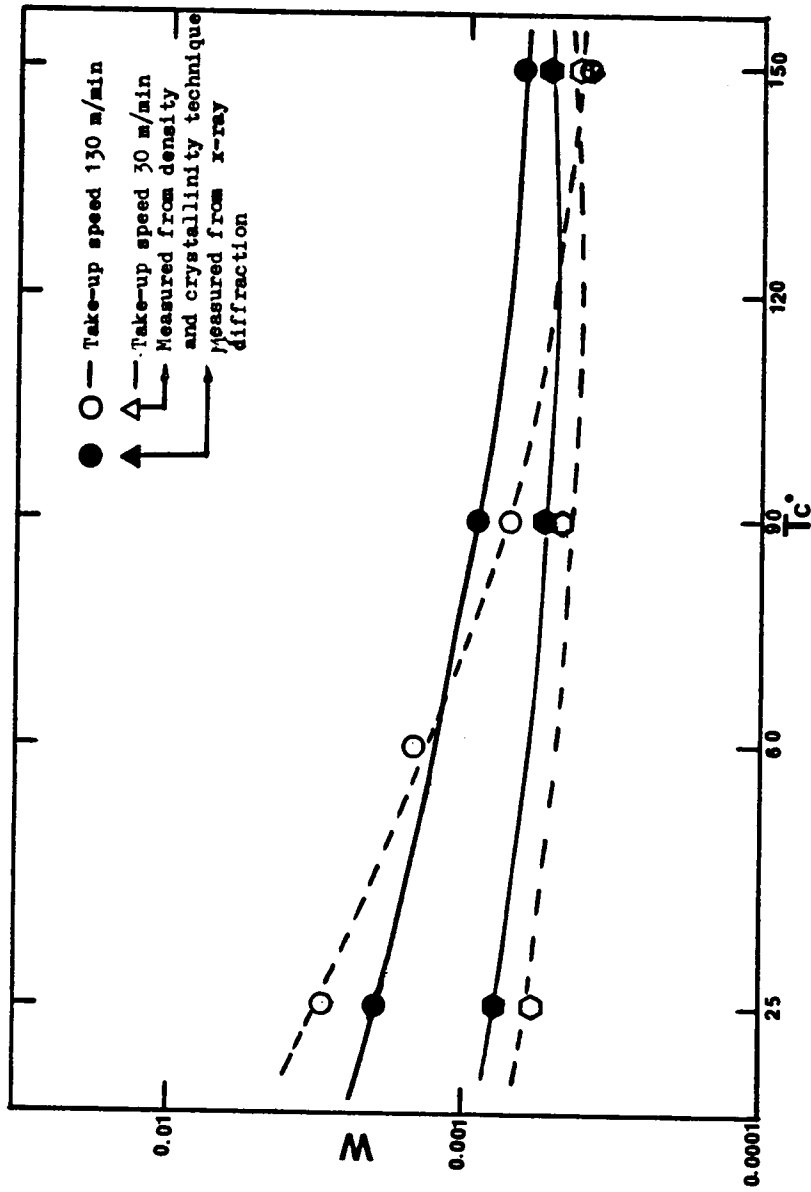


Figure IV.29. Void fraction as a function of draw temperature (effect of take-up speed).

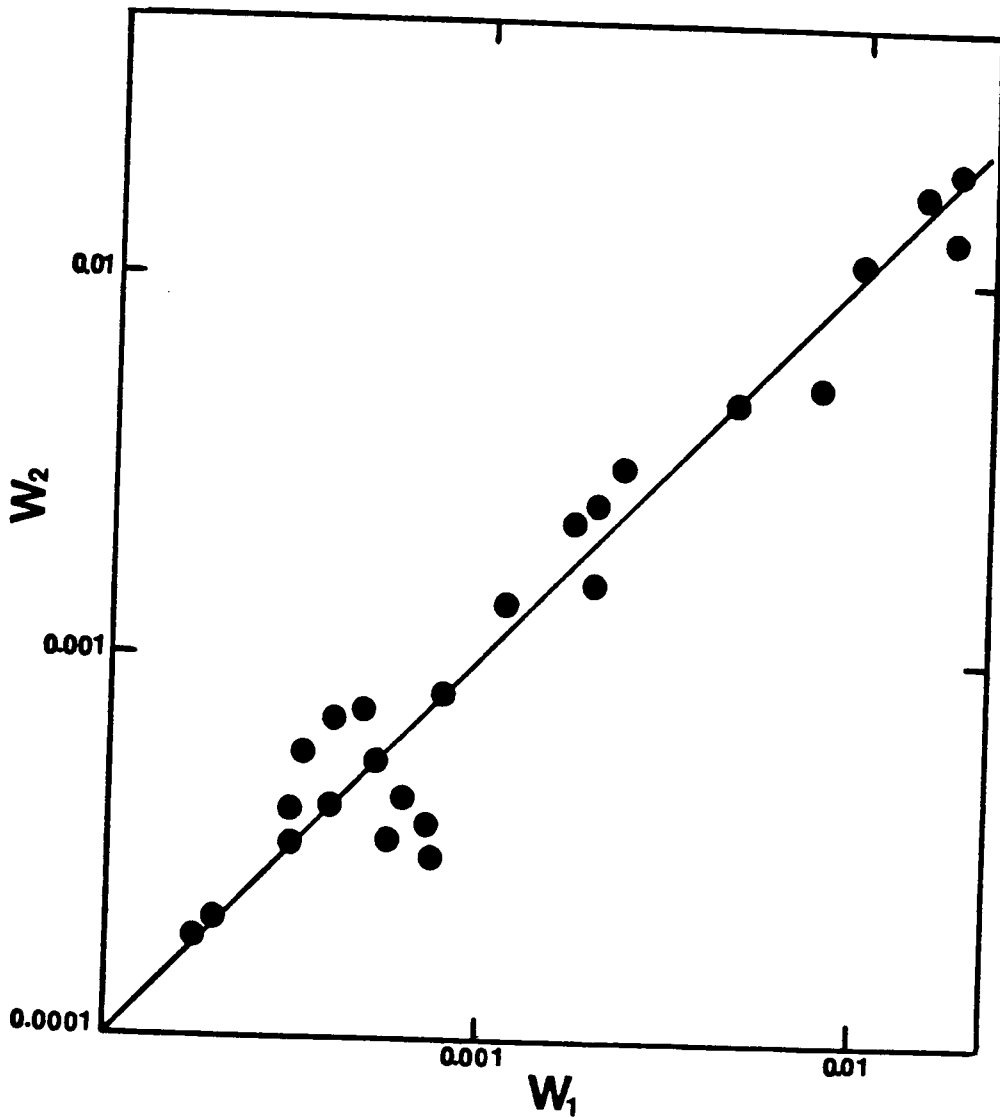


Figure IV.30. W_1 is volume fraction of microvoids measured from density and crystallinity technique. W_2 is volume fraction of microvoids measured from x-ray² diffraction.

Guinier Analysis. Two intensity profiles through the center streak scattering were taken for further analysis. One profile represented the scattering along the meridian while the second profile was along the equator. Intensity versus angle data for these profiles are plotted in Figure IV.31 and IV.32, for various selected drawn filaments.

By subjecting the scattered intensity profiles to Guinier analysis, the size, shape and number density of microvoids were evaluated. The first five intensity points of observed data, from the center streak scattering, were selected and plotted versus scattering factor S^2 (where $S = 4\pi \sin \theta / \lambda$, θ = scattering angle/2 and $\lambda = 1.5418 \text{ \AA}$, the wave length of CUK radiation). According to the Guinier approximation,

$$I(s) = I(0) \exp(-R_d^2 S^2) \quad (32)$$

When the law of Guinier is closely obeyed by an actual system, equation (32) states that a plot of $\log I(s)$ versus S^2 will be linear over a large angular range with an ordinate intercept of $\log I(0)$ and a slope of $-R_d^2$. In logarithmic form equation (32) becomes,

$$\ln I(s) = \ln I(0) - R_d^2 S^2 \Rightarrow \text{slope} = -R_d^2 \Rightarrow R_d = \sqrt{-\text{slope}}$$

this relates the angularly dependent portion of the data to the average inertial distance R_d of oriented scattering domains. Figure IV.33, shows an example of such a treatment

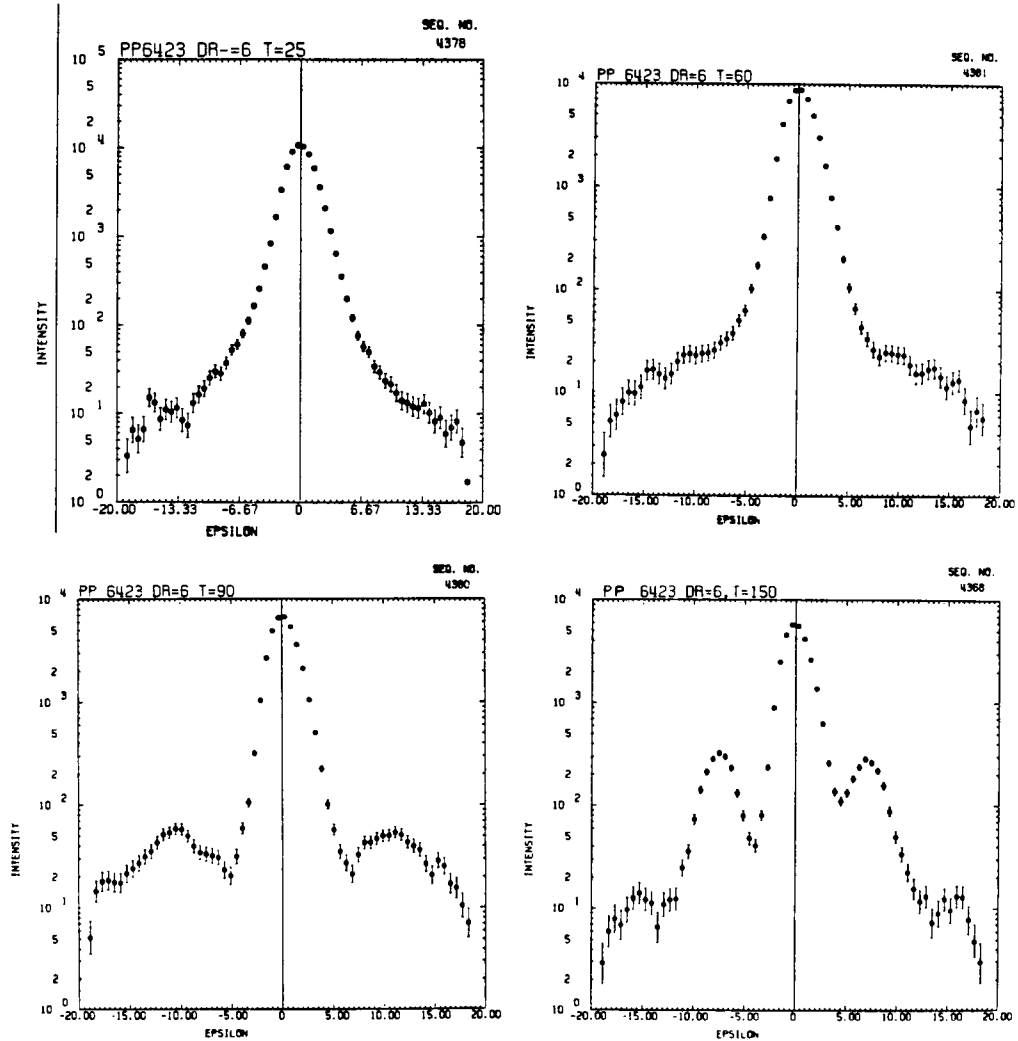


Figure IV.31. Intensity versus angle data from the center streak scattering along the meridian as a function of draw temperature.

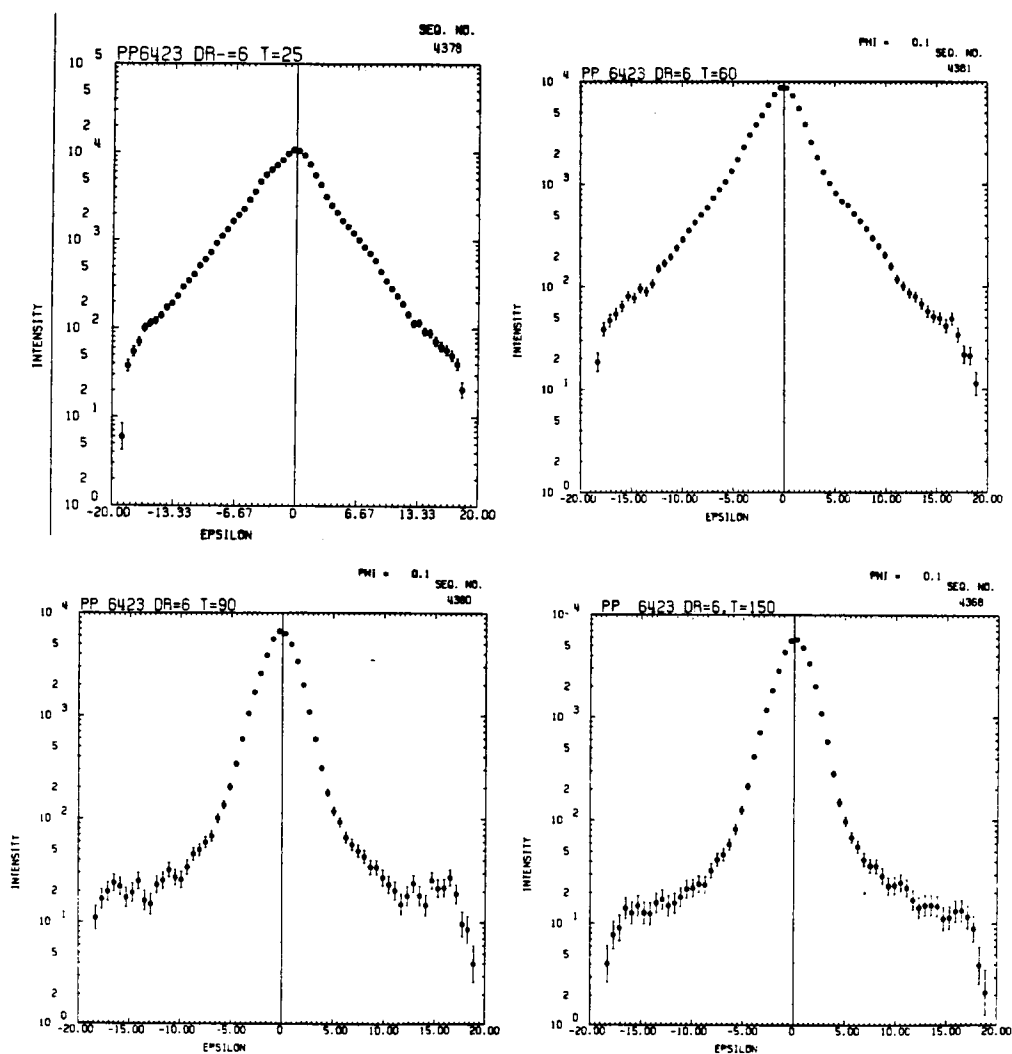


Figure IV.32. Intensity versus angle data from the profile through the center streak scattering along the equator as a function of draw temperature

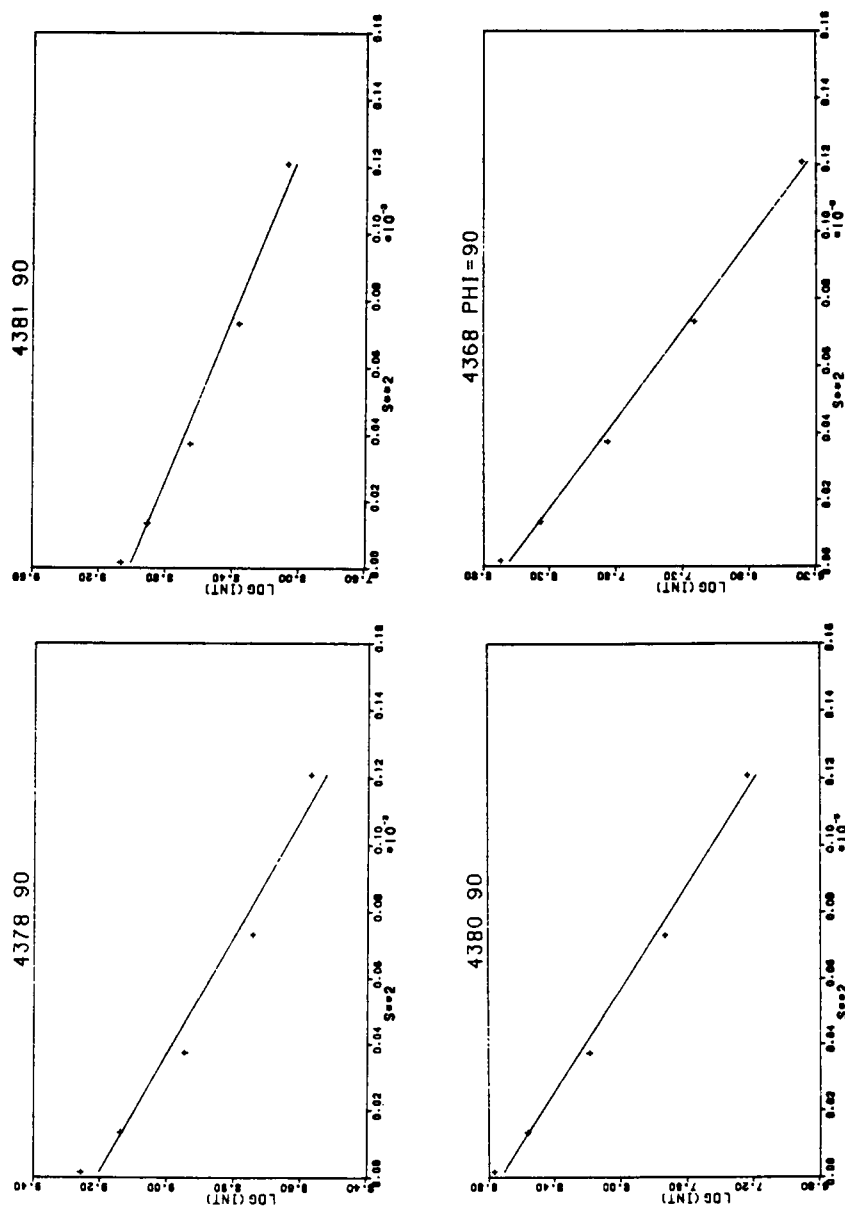


Figure IV.33. Log of intensity versus scattering factor as a function of draw temperature.

for selected drawn fibers prepared under various conditions and Table X gives the average inertial distances (R_d) and void actual dimensions measured in both scattering directions (equatorial and meridional). Void actual dimensions were calculated using a procedure given by Guinier (33), where R_d values were multiplied by $\sqrt{5}$ (Based on the assumption that the voids are ellipsoid in shape). It is apparent from this table that the void dimensions, measured from equatorial scattering are smaller than the void dimensions measured from meridional scattering for all drawing conditions. This indicates that the voids are elongated in the fiber direction and have approximately cylindrical shapes. In both scattering directions these values are smaller at low draw temperature (25°C) and they increase as draw temperature increases. Samples drawn at higher draw ratio showed smaller average void sizes but a larger number of voids for any given draw temperature. The effect of take-up velocity and molecular weight on void formation, for drawn filaments, are similar to qualitative measurements. But, the void sizes were found to be larger in lower molecular weight specimens. Also it is apparent from this table that the void number density increased with increase of draw ratio, molecular weight, take-up speed and decreased draw temperature.

Since substantial curvature exists at low scattering factor (S^2) values, from the center streak scattering of the drawn fibers, and at higher values of S^2 , the curves

TABLE X. VOID NUMBER DENSITY AND VOID DIMENSIONS FOR SELECTED DRAWN POLYPROPYLENE FIBERS

POLYMER	TAKE-UP SPEED m/min	DR(X)	DRAW T _d (C°)	R _d equatorial (Å)	VOID DIMENSIONS IN EQUATORIAL(Å)	R _d MEDIDIONAL (Å)	VOID DIMENSIONS IN MERIDIONAL(Å)	VOID NUMBER DENSITY
6423	130	6	25	75.5	168.8	120.59	269.6	4.6x10 ¹⁵
6423	130	6	60	90.9	203.2	129.20	288.9	5.5x10 ¹⁴
6423	130	6	90	113.2	253.1	137.89	308.3	5.7x10 ¹³
6423	130	6	150	137	306.3	146.09	326.7	3.4x10 ¹³
6423	130	3.5	25	81.7	182.7	117.43	262.6	1.0x10 ¹⁵
6423	130	3.5	90	111.6	249.5	140.22	313.5	3.8x10 ¹³
6423	130	3.5	150	113.14	252.9	144.1	322.2	2.8x10 ¹³
6423	30	3.5	60	94.5	211.3	129.14	288.8	1.8x10 ¹⁴
6423	30	3.5	120	113.21	253.14	134.11	299.9	2.1x10 ¹³
6423	30	3.5	150	110.42	246.8	133.88	299.4	1.7x10 ¹³
5831 106-7	130	6	25	97.66	218.4	140.09	313.0	1.4x10 ¹⁴
5831 106-7	130	6	90	99.69	222.9	161	360	5.9x10 ¹³
5831 106-7	130	6	150	112.5	251.5	173.1	387	4 x10 ¹³
5831 106-7	130	3.5	25	96.9	216.7	158.57	354.6	2.8x10 ¹⁴
5831 106-7	30	3.5	25	71	158.7	110	245.9	2.5x10 ¹³

were observed to be continuous, it can be concluded that a significant void size distribution exists. The major effect of changing the process variables is to change the void size distribution and void number density.

E. INTERPRETATION AND DISCUSSION OF FIBRILLATION

The main emphasis of this research work has been on fibrillation of polypropylene fibers. A series of compression molded polypropylene sheets have been prepared and similarly drawn for further understanding of fibrillation, which separately will be discussed in the later chapter.

SEM photomicrographs of peeled drawn fibers (Figure IV. 13 to IV.16) show that fibrillation increases with; 1) increase in draw ratio, 2) decrease in draw temperature, 3) increased orientation in the as-spun filament, and 4) increase in molecular weight of polypropylene.

A very intensive continuous equatorial scattering Figure IV.20 a,d indicate the existence of a very irregular distribution of large electron density variation in the fiber cross section. The equatorial SAXS scattering has often been interpreted as due to present of voids (3). This is further substantiated in present research work by a correlation of volume fraction of microvoids computed from the SAXS technique with microvoid fraction estimated from a combination of crystallinity (DSC technique) and density measurements Figure IV.30. However, it is apparent from SAXS

patterns in Figure IV.20 that the diffuse equatorial scattering decreases with increasing draw temperature. Patterns for drawn fibers at 150°C show a significant decrease of equatorial scattering and development of a very intense meridional diffraction (two-point pattern). The remnants of the equatorial scattering for hot drawn specimens show a decrease of voids which are strongly related to a decrease of fibrillation. This can be seen from the SEM patterns for hot drawn fibers in Figure IV.13, IV.14, IV.15.

Fibrillation can be interpreted as at least in part a result of the formation of longitudinal voids which results from extreme inhomogeneity of deformation during the transformation of the original more or less spherulitic sample into the final fiber structure. A model similar to that proposed by Peterlin (74) would seem to apply.

According to the Peterlin model depending on lamellar orientation and stacking, i.e., on the morphological properties of the starting material, the plastic deformation during drawing varies locally in rather wide limits. Each fibril contains material resulting from one stack of lamella and hence has a nearly constant draw ratio. The boundary between adjacent fibrils is more discontinuous with increasing draw ratio and eventually becomes a long cylindrical void completely separating the fibrils.

From the comparison of SAXS patterns of as-spun Figure IV.2 and drawn Figure IV.20, IV.21 fibers it is clear that

the drawing process is causing substantial changes at the spherulite and lamellar level of the fiber. The structure of the spun samples can be interpreted as a spherulitic morphology with a nearly random orientation of lamellar crystals. The patterns for drawn specimens at 25°C in Figure IV.21, a,d shows the absence of periodic structure; only equatorial scattering from voids is noticeable. This would seem to indicate that the lamellae are largely disrupted by the cold drawing. The two-point meridional spots observed in SAXS patterns in Figure IV.20, c,f corresponds to the stacks of lamellae. These meridional spots are becoming more intense with increasing draw temperature. This indicates that the drawing at higher temperature results in a more perfect lamellar structure.

Based on WAXS results Figure IV.5, to IV.9, drawing at 25°C extensively destroyed the structure including unit cell and morphology. It transforms the initially spherulitic or row structure of as-spun fiber into a fibrillar structure. The WAXS patterns Figure IV.6 show a decrease of line broadening, with increasing draw temperature which most likely result from increased coherent domain size (crystallite size). A monoclinic structure was observed for hot drawn filaments (150°C). The long spacing values were found to be greater for the hot drawn filament ($\approx 210 \text{ \AA}$) which is close to the value of $200 \text{ \AA}$ reported by Samuels (90) and Nadella, et al (65).

It is possible to investigate the fibrillation of the drawn filaments by using a combination of crystallinity measured from DSC and apparent crystallinity from density gradient column such as those shown in Figure IV.17 to IV.19 to compute the void fraction at any condition of drawing. As shown in Figure IV.17, IV.18 cold drawing (25° , 60° , 90°C) results in a decrease of filament density and its apparent crystallinity with increasing draw ratio. This abrupt change in density and crystallinity especially at the higher draw ratio (6X) was coupled with the macroscopic observation that the filament was converted from translucent to opaque. This opaque structure was observed only for cold drawn filaments which is attributed to structural elements on the order of the wavelength of light being produced by the drawing mechanism. The change from the translucent filament to the opaque filament is due to opening of the cylindrical voids parallel to fiber direction which is easily authenticated from SAXS patterns Figure IV.20, IV.21 and SEM photomicrographs Figure IV.13, IV.14.

Hot drawn samples showed much higher density accompanied by a greater tendency for recrystallization into folded chain lamellar crystal blocks stacked along the fiber axis. This can be attributed to a combination of increased level of fibrillation (void formation) and disruption of the crystal structure during cold drawing. Such interpretation is further substantiated by the comparison of void fraction and SAXS patterns at several positions shown in Figure IV.34.

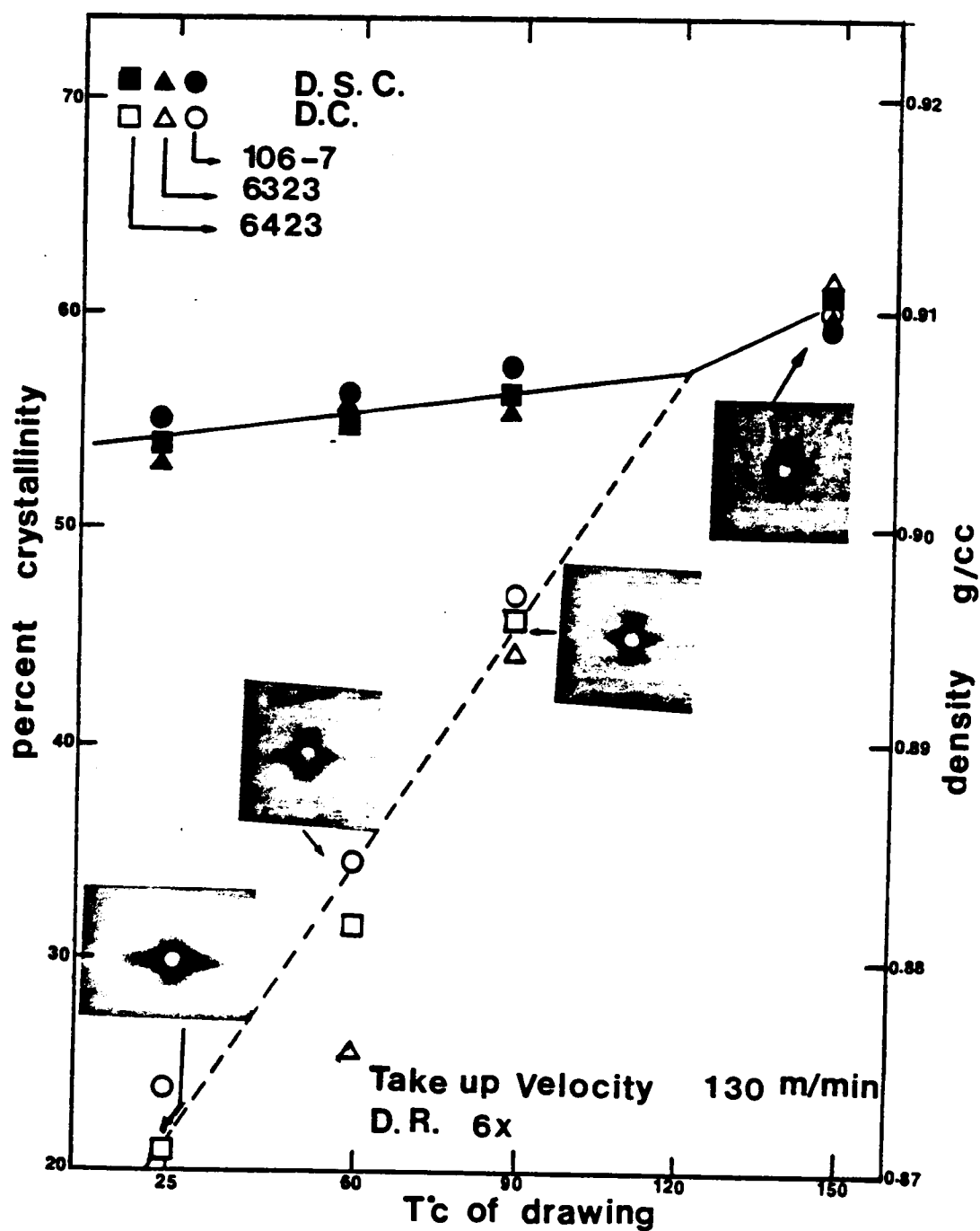


Figure IV.34. A plot of combination of crystallinity, density, and SAXS patterns versus draw temperature for drawn filaments.

The volume fraction of microvoids was computed from the quantitative SAXS measurements. These values together with void fraction measured from intensity techniques were plotted in Figure IV.26 to IV.29. The results obtained by the two techniques correlated extremely well. Figure IV.32 shows the Guinier plots of the horizontal intensity profile of the equatorial scattering, for selected samples. The slopes of the linear portions of the equatorial plots yielded average void size in the range of 150 to 250 $\text{\AA}$. Analysis of the scattering in the meridional direction resulted in values of 250 to 400 $\text{\AA}$, Table IX. Since at the higher S^2 values (above 0.12×10^{-3}) the curves of log intensity versus scattering factor S^2 were found to deviate from linearity, a void size distribution was indicated. However, the average dimensions increased with draw ratio, draw temperature, molecular weight, and spinline draw down ratio. Although the void size increased with draw temperature, the void number density decreased (Table IX). From a careful perusal of the quantitative results it can be suggested that drawing of 150°C will produce a preponderance of large voids while drawing at 25°C produces a much larger number density of voids and a shift in distribution toward small void sizes.

Individual structural parameters such as birefringence and c-axis orientation functions Figure IV.10, IV.11, IV.12 showed higher orientation values for cold drawn filaments. These observations are in good agreement with the mechanical

property results described in the next chapter and presented in Figure V.3 and V.8. The development of orientation as was indicated in Figure IV.10, IV.11, IV.12 and Figure IV.6. to IV.9 showed little variation with increasing draw temperature below about 120°C. It is apparent from these figures that below a draw temperature of 120°C a decrease in draw temperature increases fibrillation or void fraction (Figure IV. 12, IV.15) without appreciably affecting the orientation or axial mechanical properties. Above a draw temperature of about 120°C, however, both birefringence and c-axis crystalline orientation together with fibrillation decrease with draw temperature and so do the tangent modulus and tensile strength. This would seem to imply that mechanical properties mainly are a function of the orientation, and are not very much affected by changes in fibrillation alone. The significance of the 120°C temperature appears to be due to its association with the α transition or the crystal mobility temperature of polypropylene (90). The changes that occur on the spherulitic, interlamellar, and molecular levels of fiber structure during the drawing of spun fibers below the crystal mobility temperature (110°C) (the crystal absorption temperature of the dynamic mechanical spectra) were examined and compared with those observed for the same spun fiber after drawing above 110°C by Samuels (90). This subject was not studied in detail in the present experiments.

A general view of the mechanisms of drawing which form

these experiments is similar to that espoused by Peterlin (74), Sze, Spruiell and White (111), White, Dharod and Clark (118). Change in mechanical properties will be compared to those described by Samuels (90,89,85), Nadella, Spruiell and White and Kitao et al (65,52) in Chapter Five.

CHAPTER V

MECHANICAL PROPERTIES OF MELT SPUN AND DRAWN FILAMENTS

The tensile mechanical properties of both melt spun and drawn dibers were measured using a table model Instron tensile testing machine. A detailed discussion of experimental procedures was introduced in Chapter III.

Since the mechanical properties of the drawn fibers are dependent on the melt spinning and drawing variables (65), an attempt will also be made in this chapter to plot the mechanical properties of both the drawn and melt spun fibers versus birefringence to include a general correlation.

Figure V.1 shows typical stress strain behavior for the melt spun filaments of various molecular weight at take-up velocity of 30 and 130 meters per minute. The fiber modulus, yield strength and tensile strength (tenacity or breaking stress) increase with increasing take-up velocity for a given molecular weight. The fibers taken-up at a higher take-up velocity have a lower elongation to break at any given molecular weight. A distinct yield point was observed in 6323 with take-up speed of 30m/min. The yield drop and the necking elongation became less prominent as take-up speed increased. Lower molecular weight fibers exhibit higher necking elongation and 6423 (melt index 6.6) filament with take-up speed of 130 m/min did not show a significant necking

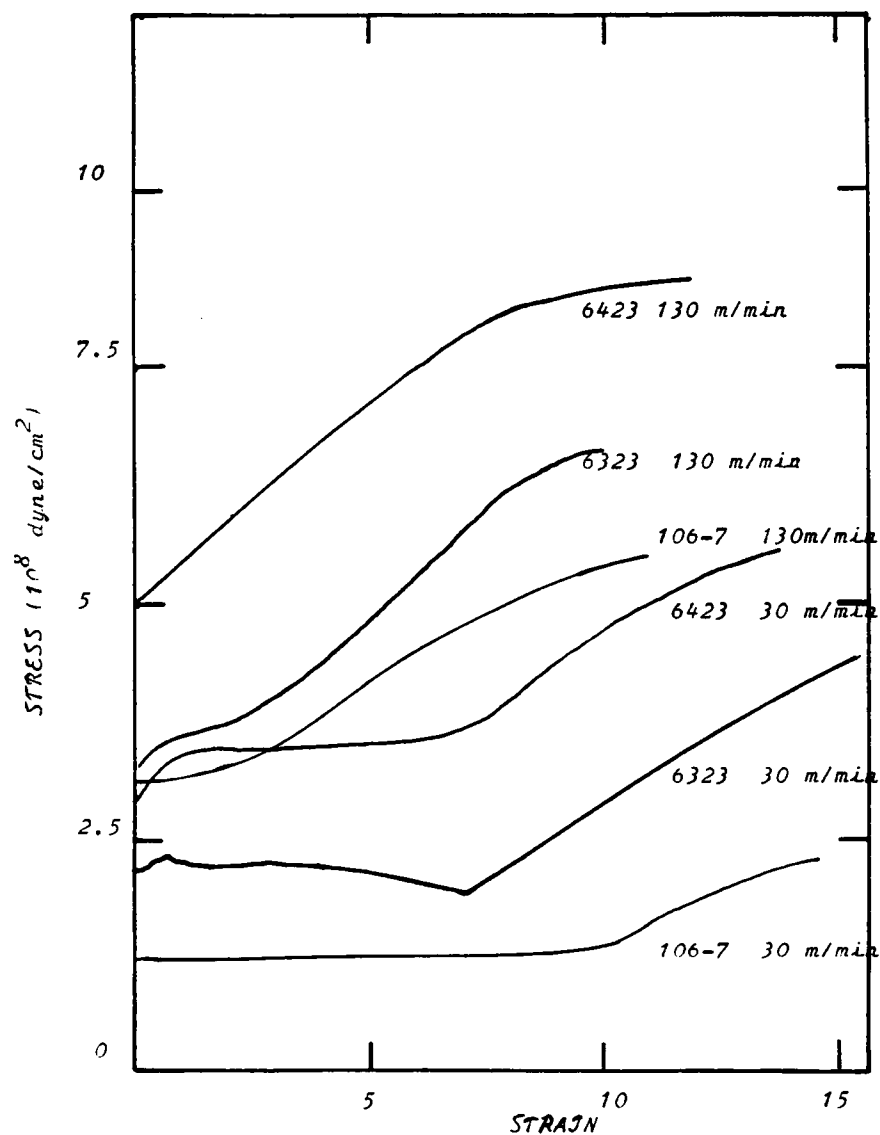


Figure V.1. Engineering stress vs strain curves for melt spun polypropylene fibers.

phenomenon.

Figure V.2 shows typical stress-strain plot of drawn and as-spun specimens. From this figure it is clear that the drawn fibers show a drastic decrease in elongation to break and a remarkable increase in breaking stress (tensile strength) in comparison with the spun filaments. The drawn samples also had much higher modulus than the as-spun samples.

Elastic Modulus

The elastic moduli of the drawn filaments were found to be dependent on the draw ratio, drawing temperature, molecular weight, and the initial structure of the filaments.

The effect of draw ratio on the modulus as a function of draw temperature is shown in Figure V.3. It is apparent that at draw ratio of 6 the modulus is higher at any given draw temperature. At a draw ratio of either 3.5 or 6 the modulus starts to decrease above a draw temperature of 120°C.

Figure V.4 shows the tensile modulus of both as-spun and drawn fibers plotted versus birefringence. The spun samples include a range of molecular weight and fibers spun at different take-up velocities. The results on drawn fibers include samples which were subjected to different draw ratio and draw temperature. It is apparent from Figure V.4 that modulus is increasing with increasing birefringence. This remarkable behavior appears to be due to the fact that the

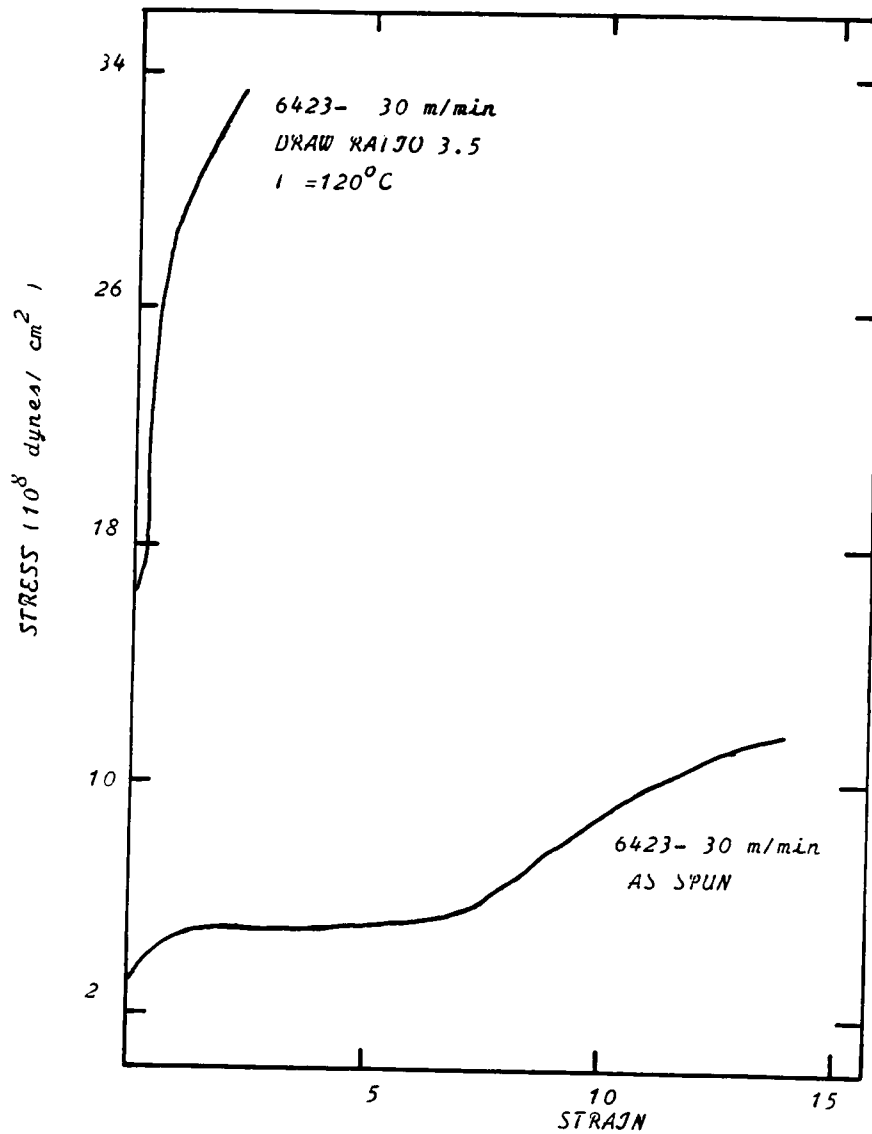


Figure V.2. Typical stress-strain curves for melt spun and hot drawn polypropylene fibers.

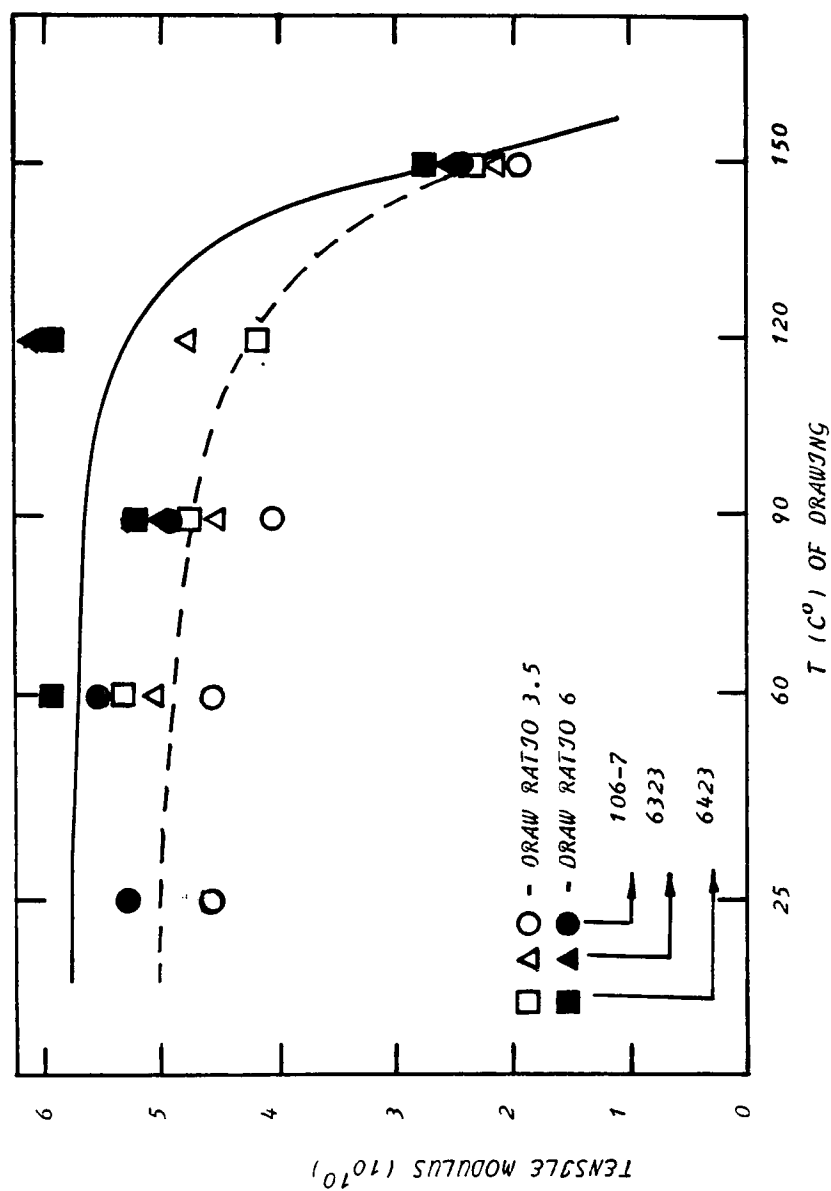


Figure V.3. Modulus vs temperature of drawing of polypropylene samples with take-up velocity of 30m/min

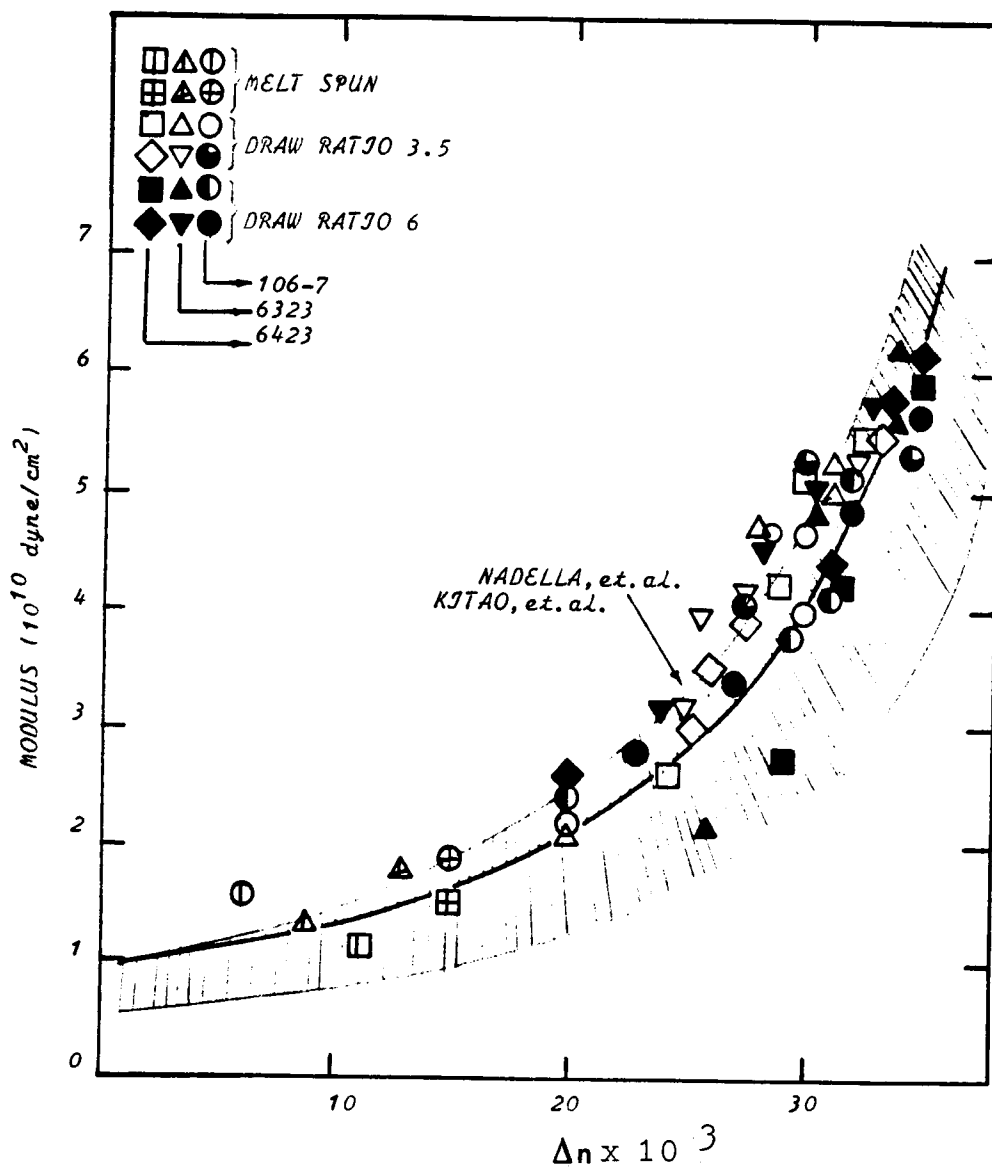


Figure V.4. Tensile modulus as a function of birefringence for melt spun and drawn polypropylene fibers.

average molecular orientation in the sample is a major factor which controls the modulus in the range of samples and variables studies.

Tensile Strength

The tensile strength of the drawn filaments also were found to be dependent on the draw ratio, drawing temperature, the initial filaments structure and the weight average molecular weight of the filaments.

Figure V.5 shows the effect of draw ratio on the tensile strength as a function of draw temperature. The effects of draw ratio and draw temperature on the tensile strength follow the same general trend as the effects of draw ratio and draw temperature on the elastic modulus Figure V.3 .

Figure V.6 shows an excellent correlation of the tensile strength of polypropylene fibers with birefringence. It is apparent that the tensile strength increases with birefringence for both as-spun and drawn samples.

Percent Elongation to Break

Table XI gives the values of percent elongation to break for melt spun filaments. From this table it can be seen that the values of elongation to break are lower for filaments provided with higher take-up velocity for each type of

TABLE XI. PERCENT ELONGATION TO BREAK FOR MELT SPUN POLYPROPYLENE FIBERS

COMMERCIAL CODE	MELT INDEX	TAKE-UP SPEED	PERCENT ELONGATION TO BREAK
6423	6.6	130	952
6423	6.6	30	1221.5
6323	12	130	1151
6323	12	30	1320
5831- 106-7	25	130	1348
5831- 106-7	25	30	1521

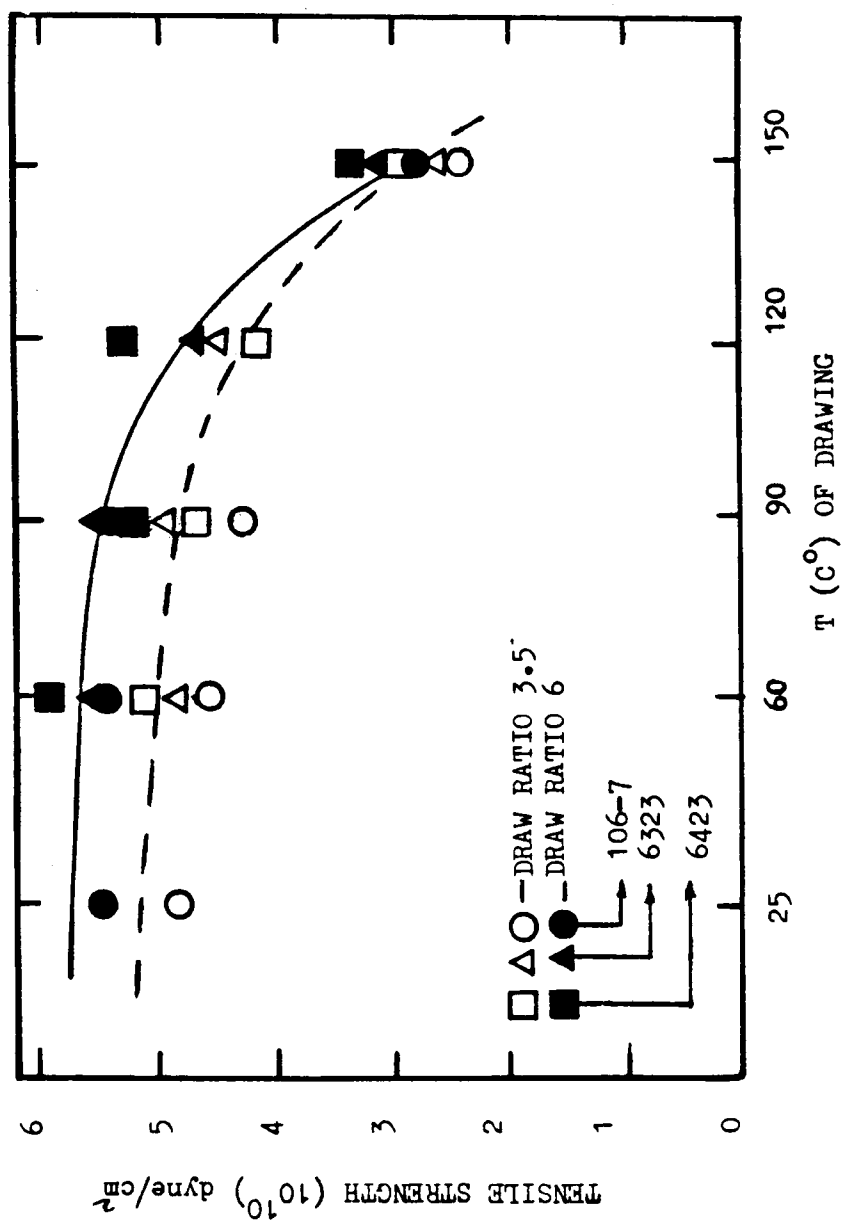


Figure V.5. Tensile strength vs temperature of drawing of polypropylene samples with take-up velocity of 30m/min

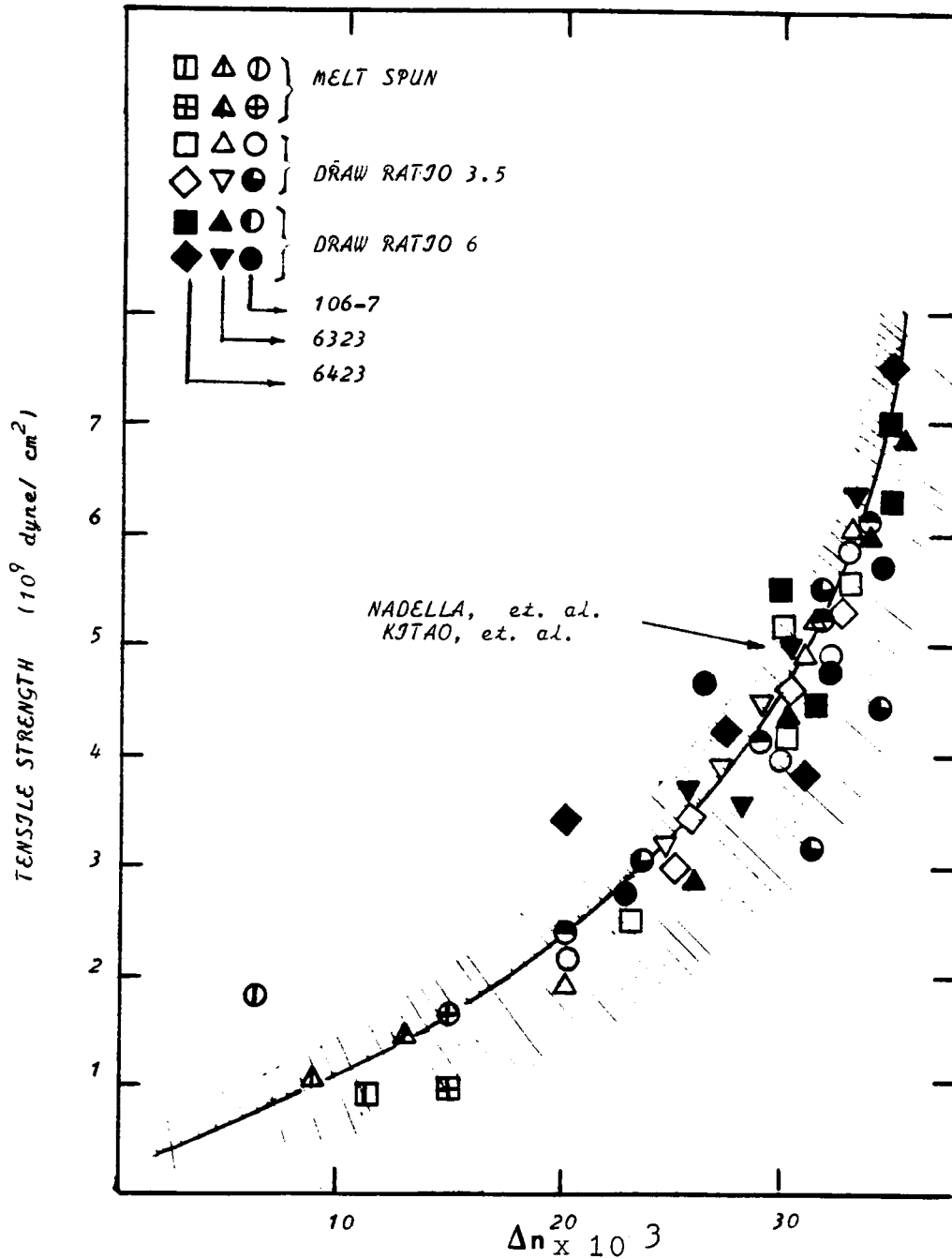


Figure V.6. Tensile strength as a function of birefringence for melt spun and drawn polypropylene fibers.

polypropylene. Also the higher molecular weight of the fiber, the less it can be elongated before it fractures.

Figure V.7 is a plot of percent elongation to break versus draw temperature for drawn fibers. The effect of draw ratio on the elongation to break is clear from this figure. The higher the draw ratio, the lower the elongation to break. The interesting point here is the effect of draw temperature on the elongation of filaments. The fibers drawn above 120°C elongated more than cold drawn samples.

Percent elongation of all various drawn fibers were plotted against birefringence in Figure V.8. It is apparent that the elongation to break correlated well with birefringence, as birefringence increases the elongation to break of drawn fibers decreases.

Discussion of Mechanical Properties of Spun and Drawn Filaments

Since the mechanical properties of the drawn filaments are partially dependent on their initial characteristics established during melt spinning, Samuels (90) suggested that the state of orientation should be used to characterize mechanical properties of fibers and films. In the present work birefringence was used to correlate the mechanical properties of both as-spun and drawn samples. In this study we compared our results with the birefringence correlation of Nadella, et al (65) and Kitao, Spruiell and White (52).

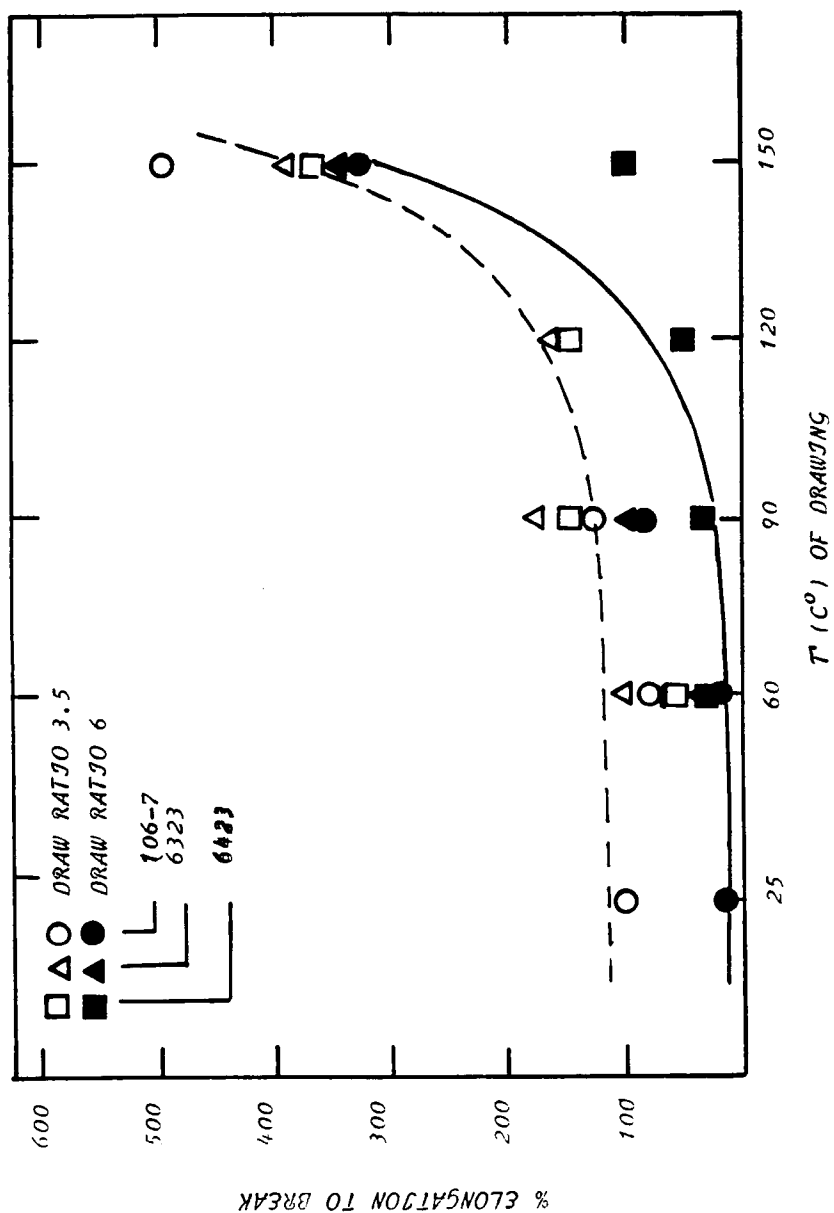


Figure V.7. Elongation to break as a function of drawing temperature for polypropylene fibers. (Take-up velocity 30m/min)

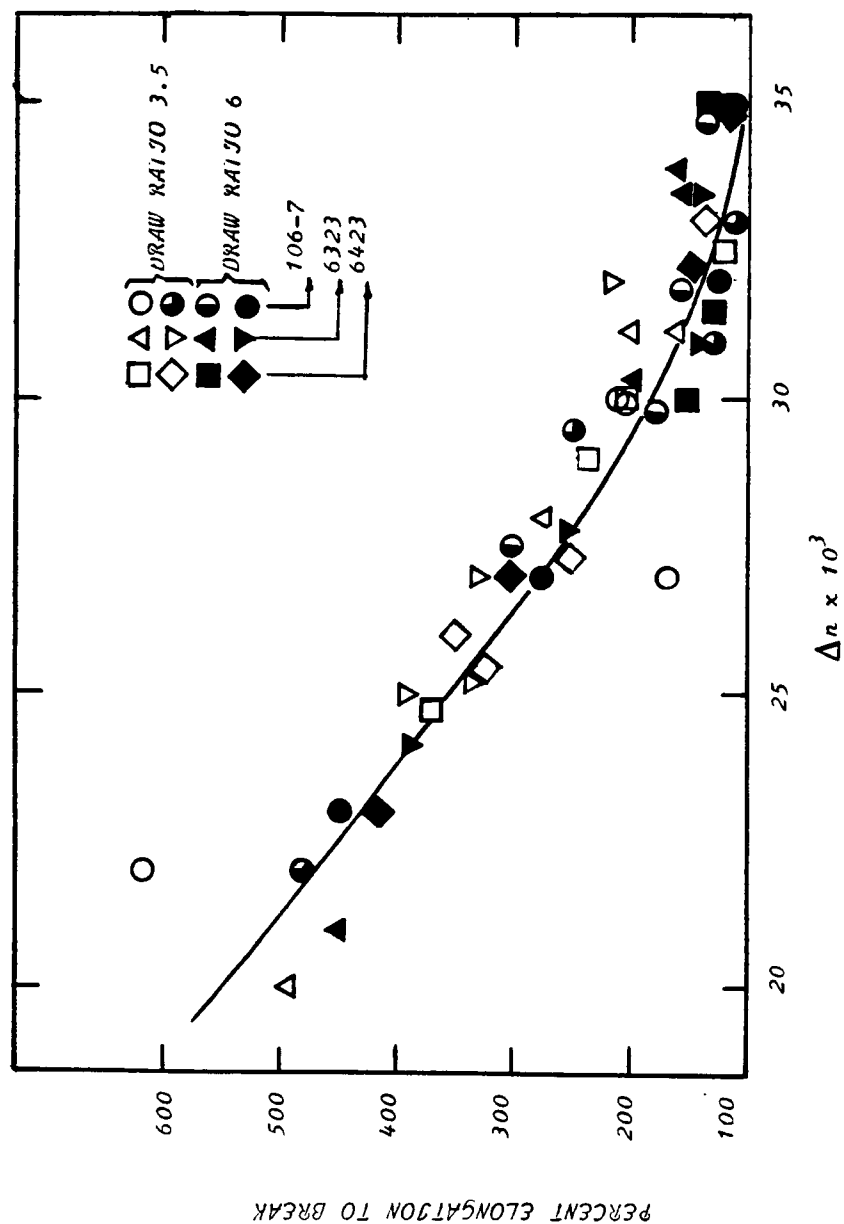


Figure V.8. Elongation to break as a function of birefringence for drawn polypropylene fibers

Clearly the present results correlate well with their results as shown in Figure V.4, V.6, V.8.

Though the mechanical properties of a fiber significantly depend on the starting structure and the thermal and mechanical process it was subjected to, knowledge of the birefringence alone can lead to the determination of these properties. This is important from a technical point of view, since the measurement of birefringence is not complicated. An attempt was made to correlate the mechanical properties with f_c , but because all the fibers are highly oriented and there is little change in the crystalline orientation from the first stage of drawing ($DR=3.5$) to the second stage ($DR=6$) of drawing while the mechanical properties are increasing significantly, the mechanical properties did not correlate well with f_c .

Samuels (90) correlated the mechanical properties of the drawn filaments with either amorphous orientation or average orientation in the fiber. The amorphous orientation factor (f_{am}) showed essentially a linear relationship with breaking stress. Since the average orientation is a weighted sum of amorphous and crystalline orientation, the present results correlate well with this quantity, because it is proportional to birefringence.

From the results in this chapter and the results obtained by Samuels (90), Nadella et al (65) and Kitao et al (52), it appears that the mechanical properties of spun and drawn

fibers could all be correlated with birefringence developed in them. This excellent behavior might be due to the fact that the average molecular orientation in the sample is a major factor which controls the mechanical properties in the range of samples and variables studied. There may be conditions under which this correlation is not valid. In particular from the curves it can be seen that the estimate of properties becomes less reliable as the birefringence increases. In this high orientation regime the properties depend on morphological features which are not necessarily accounted for in orientation measurements.

Figure V.3, V.5, and V.7 showed the effects of draw temperature on mechanical properties. Drawing at higher temperature (150°C) produces lower orientation (Figure IV.10 to IV.12) and hence lower modulus and tensile strength but higher elongation to break. This might be in part due to the thermal energy which possibly helps unfold the polymer chains.

Void fraction was plotted versus c-axis crystalline orientation function Figure V.9 in order to consider the effects of fibrillation on mechanical properties. The void fraction increases with increasing orientation but there is a drastic change of void fraction as a function of crystalline orientation with regard to draw temperature.

From the results of mechanical properties Figure V.3, V.5, V.7 and orientation Figure IV.10, IV.11, and IV.12

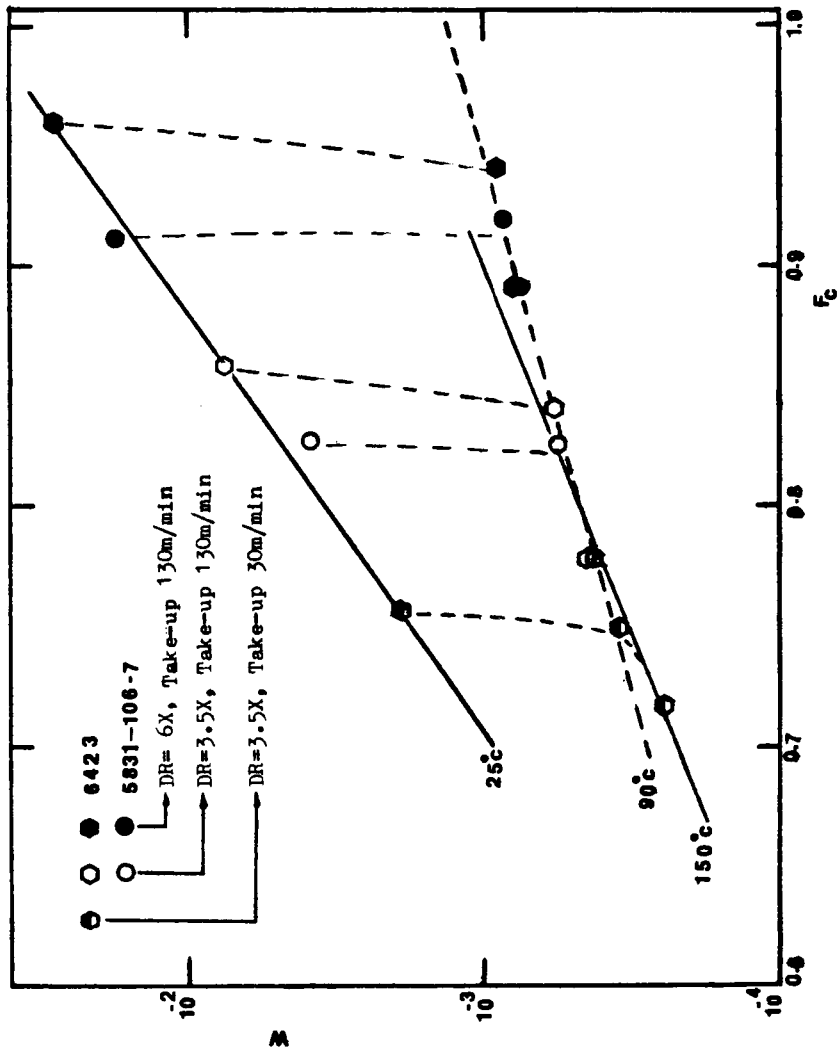


Figure V.9. Void fraction versus c-axis crystalline orientation factor for drawn polypropylene fibers

one can find that below a draw temperature of 120°C a decrease in draw temperature increases fibrillation or void fraction, Figure IV.13- IV.16, without appreciably affecting the orientation or mechanical properties. Above a draw temperature of 120°C , both orientation and fibrillation decrease with draw temperature, and so do the tangant modulus and tensile strength, This would seem to imply that axial mechanical properties of fibers are mainly a function of the orientation, and are not very much affected by changes in fibrillation alone.

CHAPTER VI

DRAWING OF COMPRESSION MOLDED POLYPROPYLENE SHEETS

In order to investigate more precisely the effect of fibrillation on the lateral direction mechanical properties, attempts were made to measure the tensile strength of fiber in the lateral direction. The drawn fibers prepared were 50 to 170 microns in diameter. Measurements of the tensile properties, in a direction perpendicular to the fiber axis of such filaments were not possible. Continued investigation lead to making a series of drawn polypropylene sheets to expand the possibility of measuring the tensile strength in a transverse direction.

The compression molding procedure was used for molding 20 cm square by 0.1 cm thick sheets. The polypropylene resins were dried at 60°C in a vacuum oven for one and a half hour. Drying the resins resulted in bubble free sheets. These dried resins were placed between hot platens at 230°C (445 F°) and heated for fifteen minutes. Once the resins were melted, a force of twenty tons was applied for a few minutes and at the same time cooling water was run through the hot platens. However, most of this twenty ton force was supported by the spacers which maintained the sheet thickness at 0.1 cm.

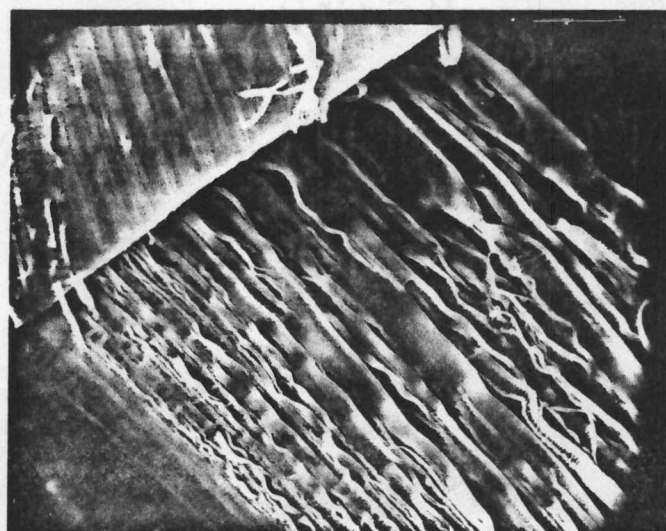
The compression molded sheets were drawn using an Instron Tensile Testing machine. Samples with one inch width

and 1.5 inch gage length, were clamped in the Instron machine and drawn by elongating them at a cross head speed of 20mm/min. Draw temperatures of 25°C (room temperature) and 150°C were selected. An oven was used for the purpose of hot drawing the sample at 150°C. Each sample was drawn just beyond the natural draw ratio and to a point near fracture of the sheet (6X).

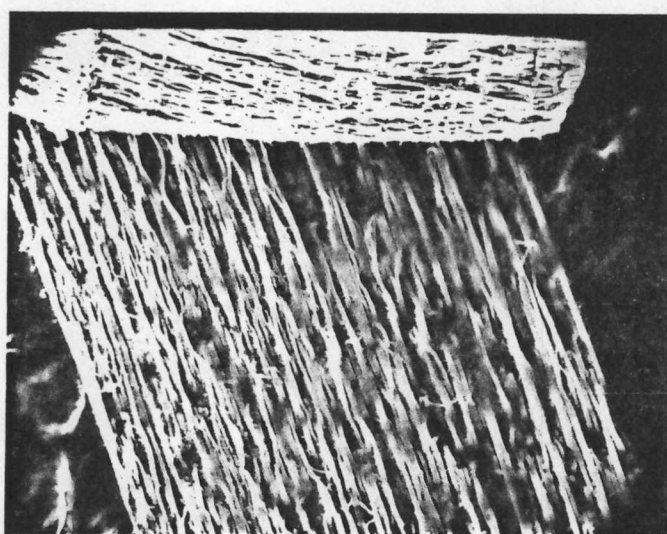
A. STRUCTURAL CHARACTERIZATION OF DRAWN COMPRESSION MOLDED POLYPROPYLENE SHEETS

Scanning Electron Microscopy

Typical SEM photomicrographs of selected drawn polypropylene sheets which were peeled after nicking with a razor blade are shown in Figure VI.1,2. Effects of draw temperature, draw ratio, and molecular weight of polypropylene were similar to those obtained from fibers, except the fibrils are much more ribbon-like for cold drawing (25°C). These observations can be seen from comparison of SEM photomicrographs in Figure VI.1, VI.2, with Figure IV.13, IV.14, for drawn fibers. As in the case of fibers, it was also found from SEM patterns of polypropylene sheets that fibrillation increases with 1) increased draw ratio, 2) increased molecular weight of polypropylene and 3) decreased temperature of drawing.



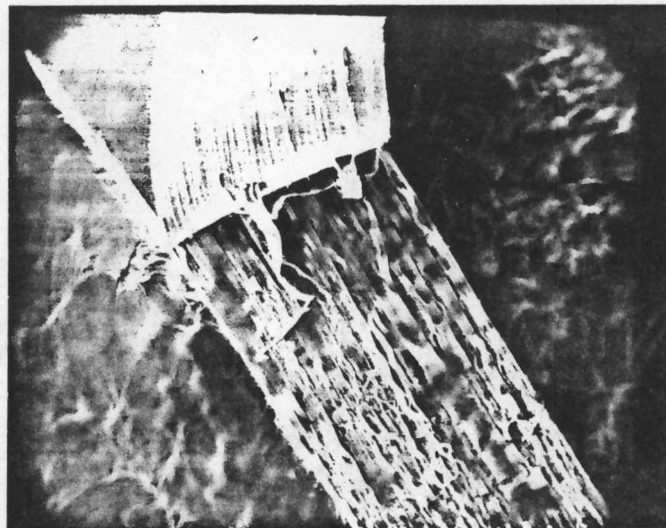
(a)



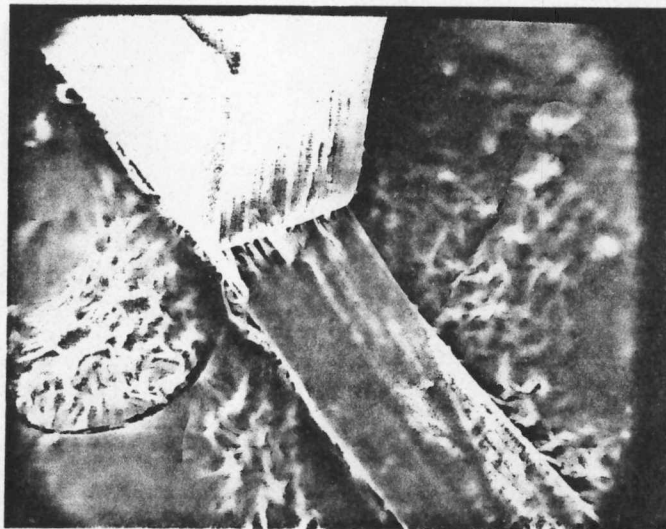
(b)

Figure VI.1. SEM photomicrographs of drawn polypropylene sheets show effect of draw temperature on level of fibrillation.

(a) Draw Ratio=6X, $T_d=25^{\circ}\text{C}$
(b) Draw Ratio=6X, $T_d=150^{\circ}\text{C}$



(a)



(b)

Figure IV.2. SEM photomicrographs of drawn polypropylene sheets for 5831-106-7 and draw ratio of 4X.

(a) Draw Ratio 4X, $T_d = 25^{\circ}\text{C}$

(b) Draw Ratio 4X, $T_d = 150^{\circ}\text{C}$

Qualitative Wide and Small Angle X-ray Scattering

The same procedures were used to obtain the SAXS and WAXS patterns of drawn sheets as were used for fibers. The wide angle x-ray patterns in Figure VI.3 give a qualitative measurement of orientation for selected undrawn and drawn polypropylene sheets at various draw temperatures. The existence of line broadening of cold drawn samples Figure VI.3-b and of sharp diffraction arcs of hot drawn specimens Figure VI.3-c, indicate similar crystalline structure changes as in drawn filaments, Figure IV.5 and IV.6 presented in Chapter IV.

The SAXS patterns for cold and hot drawn molded sheets are shown in Figure VI.4 and VI.5. The results of SAXS of drawn polypropylene sheets are similar to SAXS patterns obtained for drawn fibers.

Density and Crystallinity

Table XII gives percent apparant crystallinity (measured from density gradient column) and percent crystallinity (measured from DSC technique) for various drawn polypropylene sheets. A decrease in density was observed as draw ratio and molecular weight increased for cold drawn sheets. There was not a significant change of density with changing draw ratio for hot drawn samples. Hot drawn (150°C) sheets show significantly higher values of crystallinity (measured from

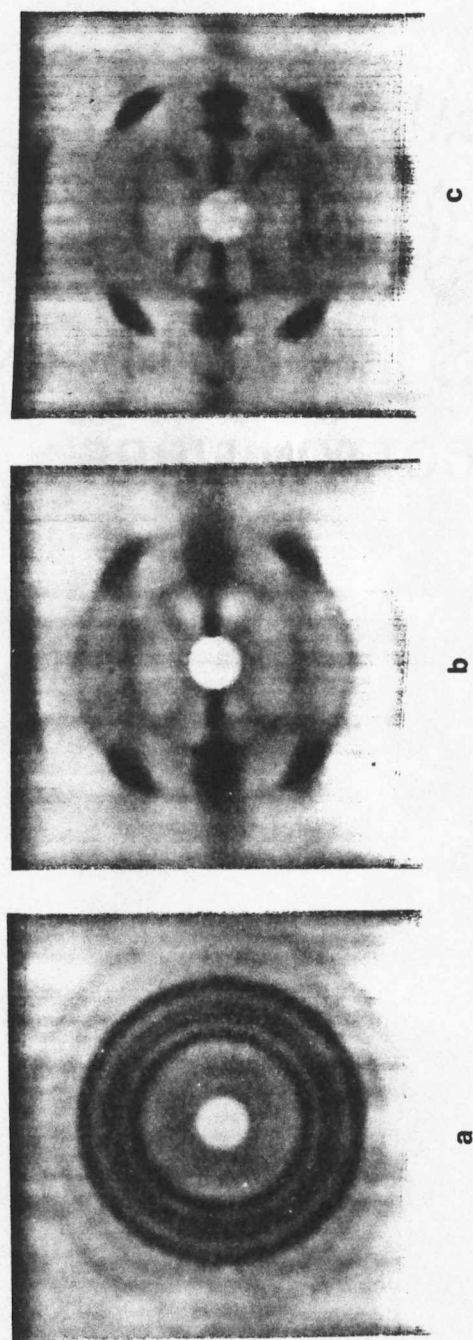


Figure VI.3. Typical WAXS patterns for compression molded sheets, cold and hot drawn polypropylene sheets.
(a) compression molded
(b) cold drawn at 25°C
(c) hot drawn at 150°C

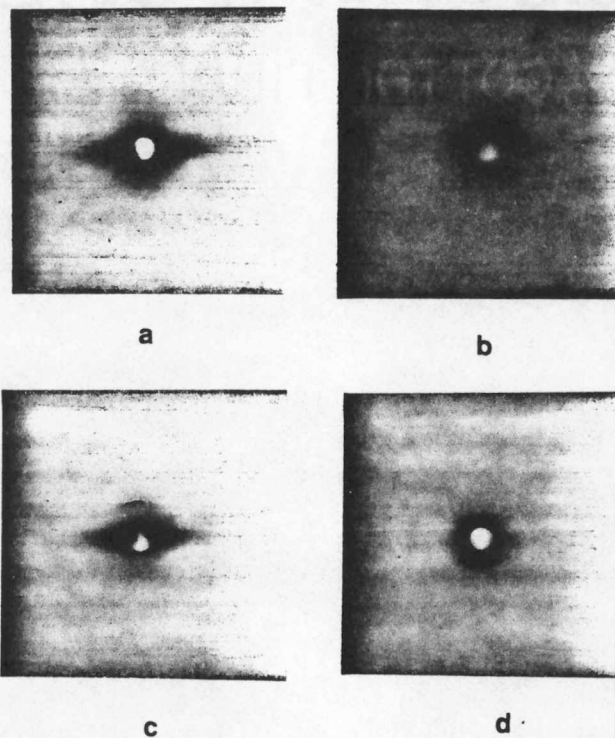


Figure VI.4. SAXS patterns of drawn polypropylene sheets with Draw Ratio 6X.

- (a) 6423, $T_d=25^{\circ}\text{C}$
- (b) 6423, $T_d=150^{\circ}\text{C}$
- (c) 5831-106-7, $T_d=25^{\circ}\text{C}$
- (d) 5831-106-7, $T_d=150^{\circ}\text{C}$

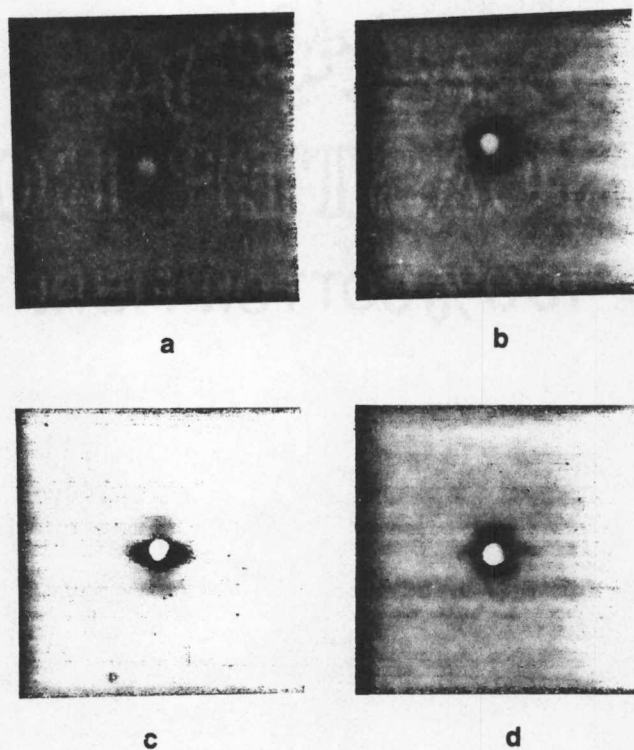


Figure VI.5. SAXS patterns of drawn polypropylene sheets with Draw Ratio 4X.

- (a) 6423, $T=25^{\circ}\text{C}$
- (b) 6423, $T=150^{\circ}\text{C}$
- (c) 106-7, $T=25^{\circ}\text{C}$
- (d) 106-7, $T=150^{\circ}\text{C}$

TABLE XII. PERCENT CRYSTALLINITY FOR DRAWN COMPRESSION MOLDED POLYPROPYLENE SHEETS

POLYMER	DRAW RATIO (x)	DRAW TEMPERATURE (°C)	PERCENT APPARENT CRYSTALLINITY (D.C)	PERCENT CRYSTALLINITY (D.S.C)
6423	6	25	35.2	50.03
6423	6	150	61.52	59.2
6423	4	25	39.9	48.99
6423	4	150	60.1	60.06
6323	6	25	34.8	51.11
6323	6	150	61.4	59.70
6323	4	25	40.3	49.3
6323	4	150	61.0	51.02
106-7	6	25	43.2	51.7
106-7	6	150	60	60
106-7	4	25	41.11	52.08
106-7	4	150	61.31	59.7

differential scanning calorimetry or density gradient column) as seen in Table XII. However, the apparent crystallinity as measured by Density technique is much lower than the values obtained by the DSC technique for the cold drawn samples. Since crystallinity measurements from DSC is independent of voids the observed different values can be attributed to voids within the samples. These results agree with the SAXS patterns Figure VI.4, VI.5 and they are consistent with those discussed for drawn fibers in Chapter IV.

Tensile Property Results

The results of the tensile property measurements carried out on drawn compression molded polypropylene sheets are presented in Table XIII and XIV. Tangent modulus and breaking strength of the drawn polypropylene sheets increases enormously in the draw direction while, elongation to break decreases with increasing draw ratio. Drawn sheets at 150°C showed a decrease of elastic modulus and tensile strength and an increased of elongation to break. These mechanical property results of drawn polypropylene sheets in draw direction (MD) were numerically similar to those obtained for drawn fibers (Chapter V).

However, from comparison of tensile properties of drawn fibers with that of drawn polypropylene sheets, one can find that drawn sheets with draw ratio 4X have a very

TABLE XIII. MECHANICAL PROPERTIES OF DRAWN POLYPROPYLENE SHEETS IN DRAW DIRECTION (MD)

POLYMER	DRAW RATIO (λ)	T_d (C°)	MODULUS dyne/cm ²	TENSILE STRENGTH % ELONGATION TO BREAK dyne/cm ²
6423	6	25	5.99×10^{10}	6.4×10^9 33.6
6423	6	150	3.6×10^{10}	3.8×10^9 255
6423	4	25	5.12×10^{10}	6.1×10^9 92.1
6423	4	150	3.2×10^{10}	2.6×10^9 293
6323	6	25	6.4×10^{10}	6.7×10^9 29.86
6323	6	150	2.81×10^{10}	3.1×10^9 212.5
6323	4	25	5.6×10^{10}	5.8×10^9 69.73
6323	4	150	3.2×10^{10}	3.9×10^9 329
106-7	6	25	5.5×10^{10}	4.8×10^9 25.4
106-7	6	150	3.3×10^{10}	3.6×10^9 25.3
106-7	4	25	4.89×10^{10}	4.3×10^9 89
106-7	4	150	3.12×10^{10}	2.49×10^9 369

TABLE XIV. TENSILE PROPERTIES OF DRAWN POLYPROPYLENE SHEETS IN TRANSVERSE DIRECTION (TD)

POLYMER	DRAW RATIO (X)	T _d (C°)	TENSILE MODULUS dyne/cm ²	TENSILE STRENGTH dyne/cm ²	% ELONGATION TO BREAK
6423	6	25	5.6 x 10 ⁸	1.7 x 10 ⁸	225
6423	6	150	9.3 x 10 ⁷	5.9 x 10 ⁷	10.2
6423	4	25	6.2 x 10 ⁸	1.3 x 10 ⁸	254
6423	4	150	8.6 x 10 ⁷	3.4 x 10 ⁷	16.1
6323	6	25	7.2 x 10 ⁸	1.66 x 10 ⁸	218
6323	6	150	8.9 x 10 ⁷	5.2 x 10 ⁷	15.6
6323	4	25	7.0 x 10 ⁸	1.6 x 10 ⁸	227
6323	4	150	7.9 x 10 ⁷	4.99 x 10 ⁷	13.2
106-7	6	25	6.8 x 10 ⁸	1.47 x 10 ⁸	246
106-7	6	150	10 x 10 ⁷	6 x 10 ⁷	19.1
106-7	4	25	6.2 x 10 ⁸	1.3 x 10 ⁸	232
106-7	4	150	6.9 x 10 ⁷	4.1 x 10 ⁷	22.1

similar mechanical properties (in draw direction) as drawn fibers with low take-up velocity (30 m/min) during melt spinning and low draw ratio of 3.5 X. This might be due to initial orientation development in both the as-spun and compression molded samples. Also the polypropylene sheets drawn with draw ratio 6X showed similar mechanical properties (in draw direction) with that of drawn fibers with draw ratio 6X, but low take-up (30m/min) during melt spinning. Such a similarity can be seen for any given draw temperature Table XIII . An attempt was made to measure the birefringence of the drawn sheets in order to correlate the mechanical properties of the polypropylene sheets with birefringence as those for fibers (Chapter V), but because of extensive opaqueness of the cold drawn sheets such measurements could not be obtained.

The drawn polypropylene sheets showed lower tangent modulus and tensile strength in the transverse direction at any given draw ratio and draw temperature compared to values measured in the draw direction (Table XIII and XIV). The elongation to break for the cold drawn (25°C) samples are somewhat higher in the transverse direction (T_d) than draw direction (MD), but for the hot drawn (150°C) sheets the reverse is true.

Correlated results were also reported by Wilchinsky (122), Dhingra et al (117), in studies of rolling effects on the mechanical property of polypropylene and Rothschild

and Maxwell (80) for polyethylene. Wilchinsky (122) reported that uniaxial rolling at room temperature resulted in an increase in tensile strength in the rolling direction, but a decrease in tensile strength and increase in elongation to break.

A closer correlation is found with the results of Dhingra, Spruiell and Clark (117) on roller polypropylene samples of the same material that was used in this study (Profax 6423). For cold-rolled samples, these authors found a higher elongation to break ratio for any percent cold work (10-75%) in the transverse direction than in the rolling direction. Since rolling and drawing processes are expected to be qualitatively similar to their effects on mechanical properties (122,80) these results appear to correlate well with those of the present work.

Dhingra et al also report the effect of cold rolled and annealing on the elongation to break in the transverse direction. They found that the elongation to break is much higher in transverse direction than those for the rolled direction. After annealing, the elongation ratio in transverse direction gradually decreased up to 100°C and then it dropped down rather drastically to very low values. Since other research workers (90,65) have reported that hot drawing produce changes which are qualitatively similar to the combined effects of cold drawing and annealing, it is of interest to compare the above behavior with that found in

the hot drawing of polypropylene observed in this study. As it was mentioned above hot drawing at 150°C substantially reduces the elongation to break in the transverse direction, when compared to the values obtained for cold drawn (25°C) samples. This is opposite to expectations based on void fraction. However these transverse mechanical properties do not seem to be controlled by void fraction per se. Furthermore, this is also substantiated by a decrease of the void number density as a function of draw temperature while the samples drawn at hot draw temperature (150°C) contain fewer but larger voids (Table X).

CONCLUSIONS AND RECOMMENDATIONS

In this chapter the major conclusions resulting from the experimental study are summarized below and are followed by recommendations for further study.

- (1) Melt fracture occurred in spinning of profax 6423 (highest molecular weight specimen among the others) with a melt index of 6.6 at extrusion temperature of 215°C . In order to avoid melt fracture, the melting temperature was increased from 215°C to 230°C .
- (2) The crystallinity and orientation of melt spun filaments increased with increasing take-up velocity and molecular weight of polypropylene. Spinning variables such as molecular weight, take-up velocity, spinning temperature, and mass flow rate effect the resulting morphology of the spun filaments.
- (3) The WAXS patterns of drawn filaments which were drawn at various conditions indicate increases in crystalline orientation brought about by drawing. Cold drawing transformed the monoclinic form of the as-melt spun filament into a more oriented but disordered structure. This was observed by exhibition of a high degree of line broadening which may be considered to result from a decrease of crystallite size and greatly enhanced lattice

strains and defects. Hot drawn samples revealed a highly oriented well formed monoclinic structure. The crystalline orientation function, f_c , was found to be in the range 0.65-0.96. The amorphous orientation factor in the range 0.3-0.45.

- (4) Density of cold drawn samples decreased with increased draw ratio, molecular weight, take-up velocity during melt spinning, and increased with draw temperature. Hot drawn samples did not show a significant difference in density with regard to draw ratio, take-up velocity and molecular weight of polypropylene.
- (5) The volume fraction of microvoids computed from the SAXS technique was found to correlate quite well with microvoids fractions estimated from a combination of crystallinity (DSC technique) and density measurements.
- (6) The volume fraction of microvoids increased with a) increased draw ratio, b) decrease of draw temperature, c) increased molecular weight, and d) increase of take-up velocity during melt spinning. The volume fractions of microvoids varied from about 0.4×10^{-3} (0.04%) to about 0.28×10^{-1} (2.8%).
- (7) The Guinier analysis showed that the average void size had dimensions of $250\text{--}400 \overset{\circ}{\text{Å}}$ parallel to the fiber axis and of order $150\text{--}250 \overset{\circ}{\text{Å}}$ perpendicular to the fiber axis. The void dimensions increased with draw ratio, draw temperature, molecular weight and spinline draw down

ratio. The void number density decreased with; 1) increased draw temperature, 2) decreased draw ratio, 3) decreased molecular weight and 4) decreased take-up velocity during melt spinning.

(8) Based on the presumption that void fraction is a measure of fibrillation, the following additional conclusions could be drawn. These observations are also consistent with SEM photomicrographs.

a) Fibrillation increase with increasing draw ratio.

b) Drawing at 25°C is accompanied by very extensive fibrillation, while the amount of fibrillation decreases as drawing temperature increases.

c) The high melt index samples showed less fibrillation than those with low melt index.

d) The filaments with low take-up velocity (30mm/min) during spinning fibrillate less comparatively than those with higher take-up.

(9) Mechanical properties such as tensile strength, tangent modulus and elongation of break of the melt spun and drawn fibers could all be correlated with birefringence measurements.

(10) It was found that mechanical properties are mainly a function of orientation and are not very much affected changes in fibrillation.

Recommendation for further study include the following:

- (1) The Guinier analysis showed the existance of a void size distribution. Continued analysis of the quantitative small angle x-ray diffraction data to determine both void size distribution and microfibril dimensions is needed in order to better characterize fibrillation and lead to the definition of a fibrillation index.
- (2) A more complete investigation of the effects of transverse deformation on fibrillated samples is needed to understand the role of both voids and fibrillation in the observed necking and elongation of the cold drawn sheets.
- (3) Further characterization of microstructure of the drawn filaments by SEM, with higher magnification and light scattering would be useful.

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