

AN INVESTIGATION OF THE ORIENTATION TEXTURE  
IN STEREOREGULAR POLYPROPYLENE FILMS

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A Thesis  
Presented to  
the Faculty of the Department of Chemistry  
Appalachian State University

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Arts

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by  
Albert Monroe Snider, Jr.  
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Albert Monroe Snider, Jr.

Approved:

*George B Miles*  
Chairman of Thesis Advisory Committee

*Eratis Williams*  
Dean of Graduate School

*James E Johnson*  
Major Professor

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To Nancy



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## ABSTRACT

The contributions of the crystalline and the noncrystalline regions to the total orientation of stereoregular polypropylene films were measured and characterized.

Films having a series of draw ratios were prepared from molten polymer.

Average crystallite orientation angles and crystallite orientation factors were obtained from densitometer measurements of flat-plate, x-ray diffraction patterns of the polypropylene films.

The average angle of total orientation and the total orientation factor were derived from the dichroic ratios observed in the polarized infrared spectra of the samples.

Utilizing the percentage crystallinities of the samples determined from density values, together with the crystallite orientation factors and the total orientation factors, the amorphous orientation factor was calculated.

This study indicates that the orientation induced in polypropylene films by drawing can be divided into two distinct parts, the contributions from the crystalline and noncrystalline regions, respectively. Drawing was observed to abruptly increase crystallite orientation with a nearly maximum value reached at a low draw ratio, followed by nearly constant values thereafter. The noncrystalline regions, in contrast, exhibited a decrease in orientation as extension began, but demonstrated an increase in orientation in the range of draw ratios where crystallite orientation made little gain.

## CHAPTER I

### INTRODUCTION

Since its first synthesis by Natta, stereoregular polypropylene has rapidly grown in importance in the production of films, fibers, and molded items. The desirable physical and mechanical properties to which this polymer owes its success can be enhanced by stretching which induces orientation of the constituent molecules. Although solid polypropylene is known to consist of crystalline and noncrystalline regions which, in turn, are known to exhibit differences in properties such as density and melting point, the differences in orientation behavior of the two regions had not been explored.

It was the purpose of this study to measure and characterize the individual contributions of the crystalline and noncrystalline regions to the total orientation. The method employed consisted of the following steps: (1) measurement of the crystallite orientation by x-ray diffraction, (2) evaluation of the total orientation from dichroic ratios observed in polarized infrared absorption spectra, (3) determination of the percentage crystallinity of films from density values, and (4) calculation of the noncrystalline contribution to the total orientation from the foregoing data.



## CHAPTER II

### REVIEW OF THE LITERATURE

#### I. PREPARATION OF STEREOREGULAR POLYPROPYLENE

Stereoregular polypropylene, a vinyl type, high polymer, is prepared by the head-to-tail polymerization of propene with the aid of a Zeigler-type, stereospecific catalyst. This catalyst is obtained by the reaction of aluminum alkyl compounds with the salts of Group IV and VI metals in a solvent, such as saturated aliphatic hydrocarbons, to which the polymer is inert. Triethyl aluminum and titanium tetrachloride are commonly used (19) (20).

The action of the catalyst appears to be complex and the mechanism is not well understood. Best substantiated is the anionic co-ordination mechanism proposed by Natta according to which successive monomeric units are added to the metal-carbon bonds of complexes (23).

#### II. PHYSICAL STRUCTURE OF STEREOREGULAR POLYPROPYLENE

Molecular structure. Stereoregular or isotactic polypropylene is characterized by linear molecules consisting of alternate asymmetric carbon atoms and methylene groups with a methyl group attached to each asymmetric center in such a way to give each the same steric configuration (20). The structure is diagrammed in Figure 1. In contrast to syndiotactic or atactic polypropylene, in which the asymmetric centers along the chain alternate in steric configuration or vary randomly, respectively, stereoregular polypropylene can undergo extensive crystallization by intimate side-by-side packing of the molecules.



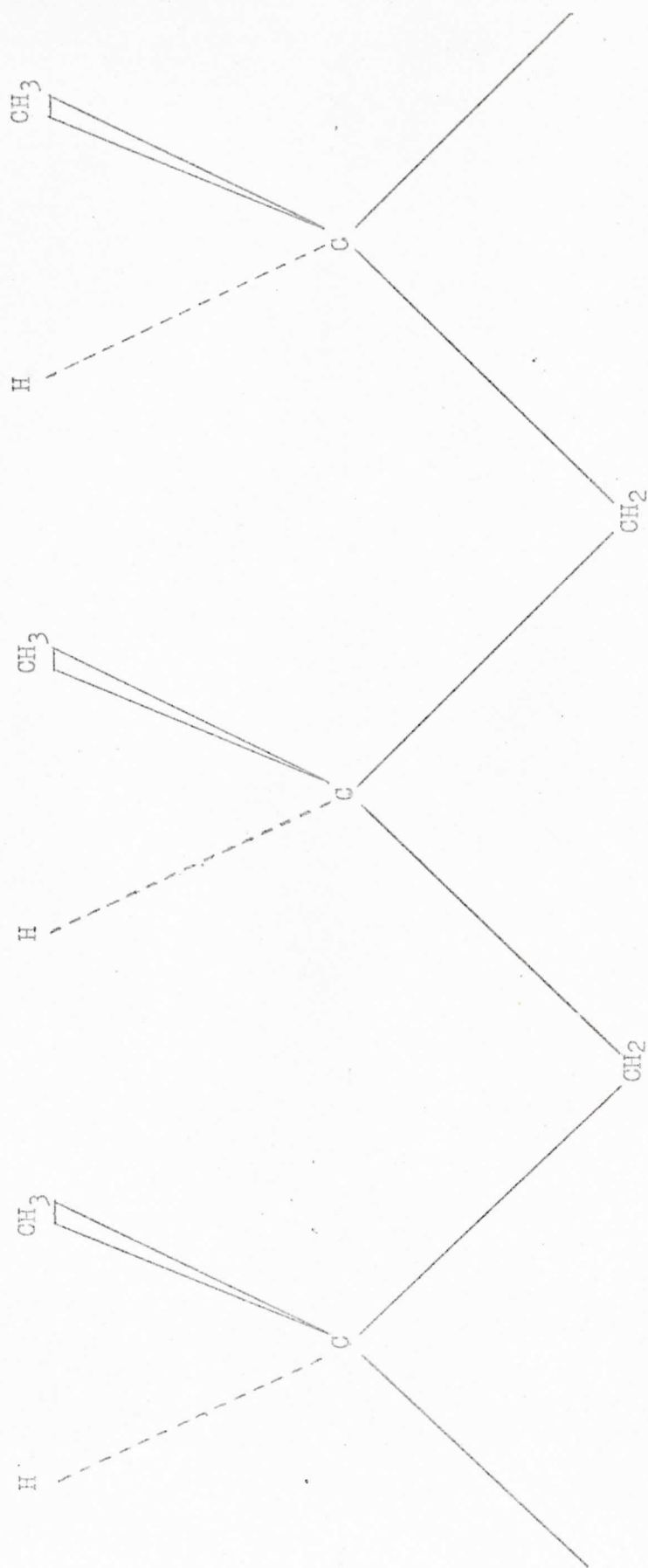


FIGURE I  
STRUCTURE OF STEREOREGULAR POLYPROPYLENE

Supramolecular structure. Solid stereoregular polypropylene is a two-phase system consisting of crystalline regions containing aligned, ordered molecules and amorphous regions containing molecules in a state of disarray (38). The exact nature of each region is still under investigation. As is the case of polymers in general, the presence of a supramolecular structure in polypropylene is indicated by x-ray diffraction patterns and by the spherulites visible with the aid of the polarizing microscope.

Several models, none of which are entirely satisfactory, have been proposed to explain the observed structure and behavior of polymers. The earliest model to gain wide acceptance, the fringed micelle model, suggests that the micelle is a relatively perfect crystal, several hundred angstrom units long, embedded in an amorphous matrix. In a crude analogy, the molecules within the micelle can be considered to lie parallel to each other like a bundle of uncooked spaghetti, whereas the molecules of the amorphous regions can be likened to snarled, cooked spaghetti. Each molecule, being much longer than a micelle, could pass alternately through several crystalline and amorphous regions.

The extended-chain crystal or micelle model, some investigators suggest, is not consistent with recent observations. First, single crystals have been prepared in which the polymer chain is believed to be folded (16) (37). These crystals are thin platelets or lamellae with a thickness of approximately 100 angstroms. Electron diffraction revealed that the polymer chain in these lamellae is perpendicular to the plane of the lamellae. Because the chain length greatly exceeds

the thickness of the lamellae, the polymer molecule must fold back and forth on itself within the crystal. A second criticism of the micelle model came from Lindenmeyer who suggested, on the basis of energy considerations, that the folded-chain crystal is more stable than the fringed crystal (16). Consequently, the folded chain model has gained support as the normal mode of the polymer crystal.

Several variations on the folded-chain, lamellar crystal theme have been proposed, each departing from the micelle model to a different degree. The most severe departure is exemplified by the defect model, primarily developed by Lindenmeyer, which regards the structure of crystalline polymers as similar to that of metals (15). The lamellae account for the crystallinity and the amorphous character is attributed mainly to dislocations within the lamellae, lamellar folds, and even voids. Although polymer chains are assumed to pass occasionally from one lamellae to another, the bridges are short and under tension, thus contributing little to the amorphous character.

Another view, the interlamellar amorphous model, takes a moderate approach according to which the stacks of lamellae are connected by amorphous regions (25). Having left a crystal, some molecules wander about before returning or entering another lamella. The extent to which the molecules reenter adjacent to the exit site or reenter at some distant point is unknown. Flory and Mandelkern have proposed models that assume the switchboard arrangements (5) (18).

Spherulites, the star-like structures visible under the polarizing microscope, are generally assumed to result from the growth of lamellae outward from the point of nucleation. During crystallization the lamellae

grow by addition of molecules to the edge, with branching of the platelet occurring frequently.

Choice of the model that is most satisfactory depends on the method of preparation of the sample being considered and its subsequent thermal and mechanical treatment. In the case of films prepared as in this study, aspects of each of the above mentioned models may be accurately applied (12).

Orientation. Because drawing is widely used to increase the strength and stiffness of polymer films and fibers, the orientation effects that accompany the drawing process are of great practical and theoretical importance. Interpretation of the changes occurring within the sample depends somewhat upon the model chosen, but the following generalizations are widely accepted.

During the drawing operation the polymer chains of the amorphous region depart from their random orientation and become progressively more nearly aligned parallel to the direction of draw. As would be expected, the vibrational modes within a chain that are either parallel or perpendicular to the chain allow the chain alignment or orientation to be monitored by means of polarized infrared radiation.

If a portion of bigger than microscopic dimensions in an undrawn polymer sample is considered, the lamellae or crystallites are assumed to lie in all possible orientations. Stretching of the sample causes the lamellae to align with their planes approaching a perpendicular orientation relative to the draw axis as the draw ratio increases (7) (24) (26). The crystallographic planes in the lamellae allow changes in orientation to be measured by means of x-ray diffraction techniques.

## III. METHODS OF INVESTIGATION

X-ray diffraction studies. Several pertinent studies of oriented polymer film using x-ray diffraction have been reported in recent years (1) (3) (4) (10) (25) (32) (34) (36).

In an undrawn polymer sample the crystallographic planes are randomly oriented so that some of the planes will by chance satisfy the Bragg's law relationship when irradiated with a beam of x-rays (3). Under these circumstances a flat-plate, x-ray diffraction pattern (fiber diagram) can be obtained which shows concentric rings similar to those seen in the polypropylene pattern of Figure 2a (see results).

If the polymer sample is stretched, the crystallographic planes tend to become oriented with respect to the direction of draw. Planes that tend to orient perpendicular to the direction of draw are referred to as diatropic planes whereas those parallel to the draw axis are called paratropic planes. In Figures 3 and 4 the diffraction spots of certain paratropic reflections are seen to both the left and right of the center, the draw axis corresponding to the long dimension of the figure. The Miller indices of the three paratropic planes responsible for these spots have been reported as (110), (040), and (130), considered consecutively from the center out. The spot at approximately  $48^\circ$  from the draw axis (corresponding to the azimuthal angle) is the superposition of diffractions from the (111), (131), and (041) planes, while the arcs near the top and bottom of the diagram are attributed to the (110) planes as a result of biaxial orientation (1).

These planes will allow diffraction of the x-ray beam if and only



if they are aligned at specific, critical angles relative to the incident x-ray beam, as dictated by Bragg's law. However, each Bragg angle allows an infinite number of azimuthal angles which, for the sake of comprehension, can be achieved by mentally rotating the plane in question around the x-ray beam axis while maintaining a fixed angle between the plane and the beam axis. In Figure 2b the Bragg angle is represented by  $\theta$  and  $\alpha$  represents the azimuthal angle.

In an undrawn sample the alignment of planes at any given azimuthal angle is equally probable. A plot of probability versus azimuthal angle would, therefore, be a straight line. Because the diffracted intensity depends on the concentration of aligned planes, a plot of intensity versus azimuthal angle of a given diffraction is also a straight line.

When the sample is subjected to drawing the random orientation of the crystallographic planes is destroyed. Preferred orientations become increasingly apparent at progressively higher draw ratios. Both the probability versus azimuthal angle plot and the diffracted intensity versus azimuthal angle plot would show a peak having increasing sharpness at the preferred orientation angle.

The relationship of diffracted intensity to plane orientation provides a method for the quantitative evaluation of the crystallite orientation. An important approach to this measurement is the method of P. H. Hermans (9). Hermans suggested a crystallite orientation factor,  $F_c$ , calculated by using the formula,  $F_c = 1 - \frac{3}{2} \overline{\sin^2 B}$ , in which  $\overline{\sin^2 B}$  was defined by the expression,  $\overline{\sin^2 B} = \frac{\int dB \sin^3 B J(B)}{\int dB \sin B J(B)}$ .  $J$  is the diffracted intensity of a diatropic plane at azimuthal angle  $B$ , measured from the axis.

In this study, because of the greater intensity and sharpness of the paratropic planes than the diatropic planes, the paratropic planes were employed. It was assumed that the course of orientation of the paratropic planes corresponds to the course of orientation of the diatropic planes. Also, it was assumed that the sine square of the average angle of orientation will not be greatly different from the  $\overline{\sin^2 B}$  given by Hermans (9).

Studies of dichroism with polarized infrared radiation. Several studies of orientation in stereoregular polypropylene utilizing polarized infrared radiation have been published (6) (13) (14) (29) (30). These studies have provided information on band assignments, relative intensity, and polarization effect. Of particular interest in this study is the  $840 \text{ cm}^{-1}$  band which shows pronounced parallel polarization effects, is crystallinity sensitive, and appears to result from carbon--carbon band stretching or  $\text{CH}_3$  wagging or rocking (13) (23).

Molecular vibration involving electrically polarized bands produce an oscillating dipole which is called a transition moment (4). A definite relationship exists between transition moment of a given vibration and the rest of the molecule. In the case of high polymers the transition moment can be either parallel or perpendicular to the main chain backbone and be of interest in orientation studies. When the frequency of the incident infrared radiation coincides with that of the molecular vibration, energy absorption can occur. The magnitude of the interaction is a function of the square of the cosine of the angle between the transition moment of the molecular vibration and the electric vector of the radiation.

Consequently, maximum absorption occurs when the electric vector of the polarized infrared radiation is parallel to the transition moment vector.

In a stretched high polymer film the molecular chains tend to line up parallel to the direction of draw (6). Thus, infrared radiation that has been plane-polarized in a known direction can be used to determine which absorption bands have their transition moments preferentially parallel to the chain and which are preferentially perpendicular to it. More important in the application at hand is the fact that the extent of orientation of the chains can be determined from the proper absorption data.

The dichroic ratio,  $R$ , defined by the formula,  $R = \frac{A_{\parallel}}{A_{\perp}}$ , where  $A_{\parallel}$  and  $A_{\perp}$  represent the absorbances when the electric vector of the polarized infrared radiation is aligned parallel and perpendicular, respectively, to the draw axis, is a useful measure of orientation (38). When the polymer chains are randomly oriented, as is the case in undrawn films, their transition moment vectors have a summation of zero yielding a dichroic ratio of unity. Drawing aligns the transition moments producing a vector summation that is no longer zero and thus a dichroic ratio that varies with the extent of draw.

The average orientation angle,  $\theta$ , which represents the angle between the group transition moment vector and the draw axis, is calculated according to the formula:  $\theta = \cot^{-1} \sqrt{\frac{R}{2}}$ , derived from the preceding equation (F).

Because the polypropylene chains pass through both crystalline and amorphous regions, the value of  $\theta$  represents the total average orientation angle in the sample, inclusive of crystalline and amorphous orientation.



Crystallinity determination. Methods for determining the percentage crystallinity of stereoregular polypropylene include an x-ray method developed by Natta, Corradini, and Cesare (37), several infrared absorption methods developed by Heinen, Luonge, Brader, Quynn, and others (2) (8) (17) (27), and a density method used by Quynn (27).

The density method, used in the current study, allows calculation of the percentage crystallinity of each sample from its experimentally determined density and the densities of completely amorphous and completely crystalline stereoregular polypropylene reported by Natta (37) (38). The following formula,  $\%X = \frac{D_c (D_x - D_a)}{D_x (D_c - D_a)} \times 100$ , expresses the relationship between percentage crystallinity, %X, and the densities of the completely amorphous,  $D_a$ , and the completely crystalline,  $D_c$ , polypropylene, respectively. The value of  $D_c$  was reported as 0.936 g/cm and  $D_a$  was stated as 0.859 g/cm.

## CHAPTER III

### EXPERIMENTAL

#### I. FILM PREPARATION

Pellets of stereoregular polypropylene, Escon 125, obtained from Enjay Chemical Company, were used in this study. A 0.5 g sample of the pellets, placed on a 4" x 4" aluminum plate, was melted at approximately 168°C under a nitrogen atmosphere to minimize oxidative degradation. A second metal plate, preheated to the same temperature, was pressed down upon the melt to produce a thin film of the desired thickness. The pressed melt was subsequently dropped into a beaker of water at about 10°C. Finally, with the aid of a stream of water, the film was gently peeled from the metal plates. The films thus prepared were stored to await orientation treatment.

#### II. ORIENTATION OF POLYPROPYLENE FILMS

Film strips, 0.5 in wide, were marked along each edge at uniform intervals and clamped at both ends in a drawing frame. Heat was applied to the film strip by means of a heat lamp until a thermometer 0.5 cm below the strip indicated a temperature of 95-100°C.

Each sample was drawn, individually, at a rate of about 50 cm per min, then air-cooled at room temperature, and subsequently maintained at the extended length for one hour. After removal of the film from the frame, twenty-four hours was allowed to elapse before final spacings of the reference marks were measured. The draw ratio, defined as the

final length divided by the original length, was calculated for each selected segment. This data from variously oriented samples is shown in Table I.

### III. X-RAY DIFFRACTION STUDIES

Flat plate x-ray diffraction patterns were obtained for the oriented films having various draw ratios. This was done by placing the film in a microsample holder so that the axis of draw of the film was vertical and parallel to the flat plate cassette containing Ilford, high speed x-ray film. The collimated beam of nickel-filtered, copper  $K\alpha$  radiation obtained with a General Electric XRD-5 x-ray diffraction unit with a copper target x-ray tube operated at 35 kV and 1.5 mA impinged on the sample for 45 minutes.

The film was removed from the cassette, developed according to recognized procedure, washed and dried.

The developed films were centered on the stage of a Nonius microdensitometer and azimuthal scans of the intensities of the (110) reflection performed. These data were recorded and plots of intensity versus azimuthal angle were made. After background correction, the average angle of crystallite orientation,  $B$ , was determined. This parameter is defined as the breadth of the peak at half-maximum intensity. These angles of orientation were recorded. Finally, the crystallite orientation factor,  $F_x$ , for each sample was calculated in accordance with the following equation derived by P. H. Hermans (9):  $F_x = 1 - \frac{3}{2} \sin^2 B$

Intensity and azimuthal angle data for representative scans are

given in Table II. Table III presents the average angles of crystallite orientation and Table IV displays the crystallite orientation factors. Selected graphs of the data are shown in Figures 5 through 9.

#### IV. STUDIES OF DICHOISM WITH POLARIZED INFRARED RADIATION

In order to obtain information on the total orientation (crystallite plus amorphous) in the samples, polarized infrared absorption spectra from 600-4000  $\text{cm}^{-1}$  were obtained. The optimum gain, period, scanning speed, and slit program were set for double-beam operation.

By means of a microsample holder, the samples were mounted, in turn, at the focal point of a beam condenser used in association with a silver chloride polarizing element and a Beckman, IR-7, infrared spectrophotometer. Consecutive scans were obtained for each sample with the electric vector of the polarized infrared radiation first parallel to the direction of extension of the film and then perpendicular to the draw axis.

Absorbancies at 840  $\text{cm}^{-1}$  for parallel and perpendicular scans, like those determined by the base-line method and are given in Table V. The dichroic ratios,  $R$ , for the various samples were calculated from these data in accordance with the relationship  $R = \frac{A_{\parallel}}{A_{\perp}}$ , Where  $A_{\parallel}$  and  $A_{\perp}$  represent the parallel and perpendicular absorbances, respectively. Also, the average angle of total orientation,  $\theta$ , was determined from the equation  $\theta = \cot^{-1} \frac{\sqrt{R}}{2}$ . Finally, the total orientation factor,  $F_{\parallel}$ , was calculated from the Hermans equation mentioned previously:  $F_{\parallel} = 1 - 3/2 \sin^2 \theta$ . The values of  $\theta$  and  $F_{\parallel}$  are given in Tables IV and VI, respectively. Graphical representations are shown in Figures 12 and 13.

## V. DETERMINATION OF CRYSTALLINITY

The density of each polymer film sample was determined by a flotation method. Water and Fisher Certified 95% ethanol were mixed in such proportions that a given polymer sample would remain suspended at any chosen depth in the liquid. By means of a pycnometer, the density of the liquid was then determined. This density value was recorded as that of the polymer film. In these measurements, a constant temperature of 25.0°C was maintained by means of a Precision Scientific Co. constant temperature water bath. The densities,  $D_x$ , thus measured were used to calculate the percentage crystallinity,  $\%X$ , in the polymer films by utilizing the following equation:  $\%X = \frac{D_c (D_x - D_a)}{D_x (D_c - D_a)} \times 100$ . The densities of totally amorphous polypropylene,  $D_a$ , and total crystalline polypropylene,  $D_c$ , have been reported by Natta as 0.856 g/cm<sup>3</sup> and 0.936 g/cm<sup>3</sup>, respectively.

Densities and crystallinities are presented in Table VII. A plot of percentage crystallinity versus draw ratio is shown by Figure 14.

## VI. DETERMINATION OF AMORPHOUS ORIENTATION FACTORS

The primary purpose of this investigation was to obtain information on the contribution, if any, of the disordered regions to the orientation induced by drawing.

Based on the assumption that the total orientation factor consists of additive contributions from both the crystalline regions and the disordered regions, the following equation should be valid:  $F_T = XF_C + (1-X) F_a$ . The terms  $F_T$ ,  $F_C$ ,  $F_a$  and  $X$  represent total, crystallite, and amorphous orientations and fractional crystallinity, respectively.

The data for  $F_r$ ,  $F_c$ , and  $F_a$  are given in Table IV. Figure 15 presents a plot of the amorphous orientation factor versus draw ratio.



## CHAPTER IV

### RESULTS AND DISCUSSION

#### I. X-RAY DIFFRACTION STUDIES

Visual inspection of the developed flat-plate x-ray films for each of the samples listed in Table I readily revealed a pronounced relationship between draw ratio and crystallite orientation. The concentric rings apparent in the unoriented sample convert to arcs which decrease in angular spread as the draw ratio is increased. This transition is apparent in Figures 2a, 3, 4 and is also revealed in the intensity data of Table II obtained from the azimuthal scan by means of the microdensitometer. Representative plots of these data are found in Figures 5 through 7.

The average crystallite orientation angles, defined earlier, are presented in tabular and graphical form in Tables III and Figure 8, respectively. Figure 8 indicates a rapid drop in average crystallite orientation angle until a draw ratio of approximately 2.4 is reached, at which point the slope abruptly decreases and the curve appears to approach zero angle orientation asymptotically. The crystallite orientation factors, displayed in Table IV and Figure 9, similarly demonstrate a relatively large gain at low draw ratios, with an abrupt change to nearly constant values above the draw ratio 2.4. Consequently, it is clear that most of the crystallite orientation occurred during the early stages of draw, and little occurred thereafter. The importance of this observation will emerge in later discussions.

TABLE I

THE LENGTHS AND DRAW RATIOS OF THE EXPERIMENTAL  
SAMPLES OF STEREOREGULAR POLYPROPYLENE FILM

Sample	Original length, cm	Final length, cm	Draw ratio
4	0.500	0.500	1.00
5	0.318	0.750	2.36
7	0.500	1.75	3.50
8	0.500	2.00	4.00
9	0.500	2.13	4.26
11	0.500	2.40	4.80
2	0.318	1.55	4.88
3	0.318	1.78	5.61
1	0.318	1.84	6.08
6	0.500	3.25	6.50
12	0.500	3.28	6.56
10	0.500	3.83	7.66



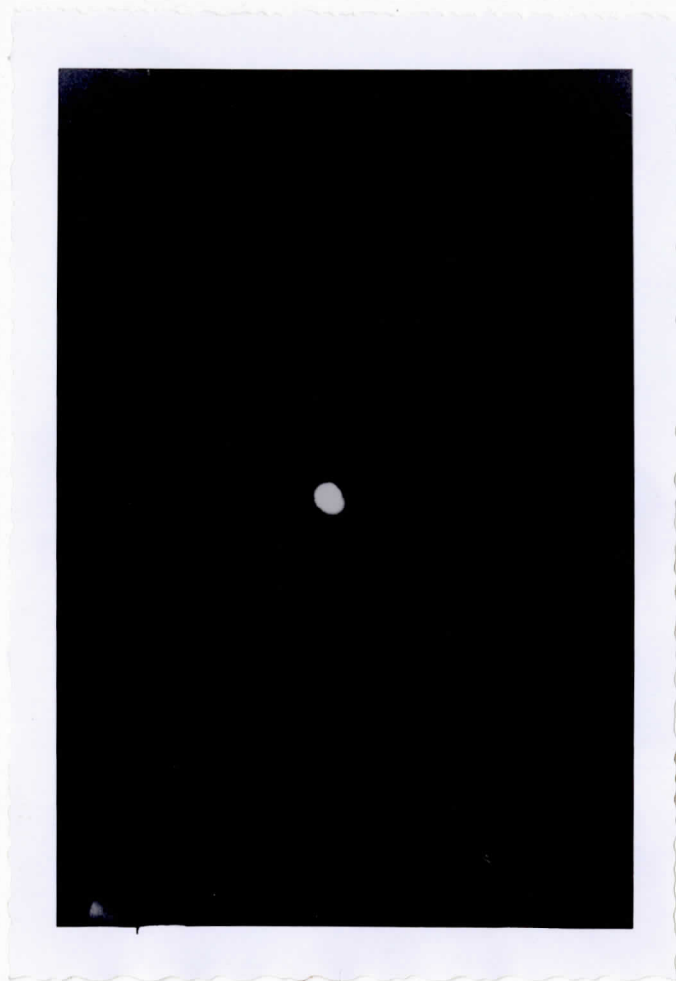


FIGURE 2a

FLAT-PLATE X-RAY DIFFRACTION PATTERN OF A STEREOREGULAR  
POLYPROPYLENE FILM--DRAW RATIO 1.00

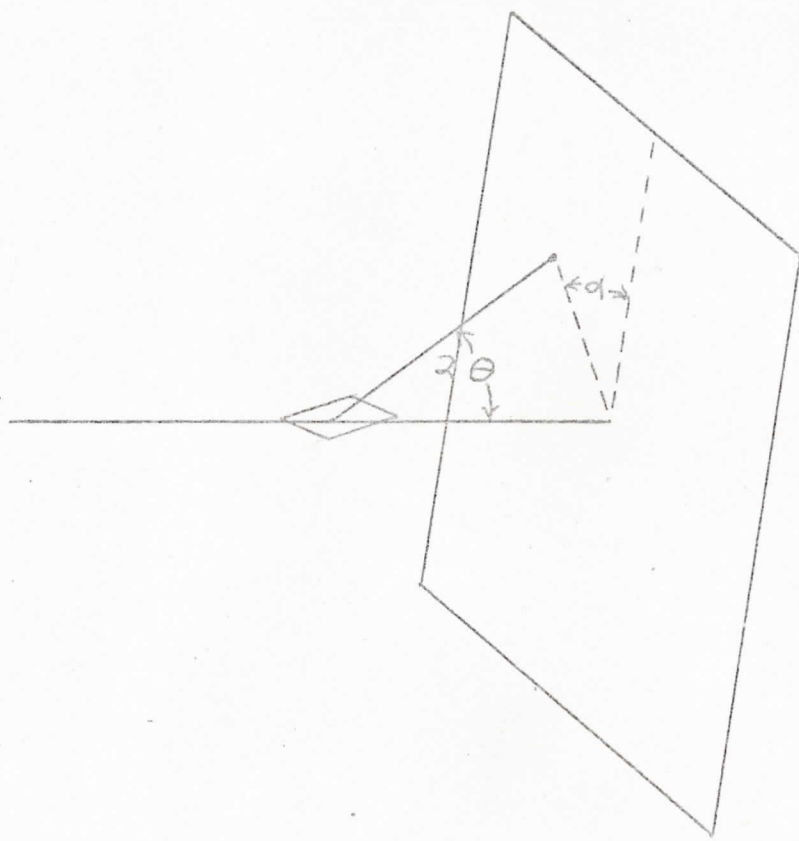


FIGURE 2b  
BRAGG ANGLE,  $\theta$ , AND AZIMUTHAL ANGLE,  $\alpha$   
RELATIVE TO FLAT-PLATE AND X-RAY BEAM



FIGURE 3

FLAT-PLAT X-RAY DIFFRACTION PATTERN OF A STEREOREGULAR  
POLYPROPYLENE FILM--DRAW RATIO 3.50

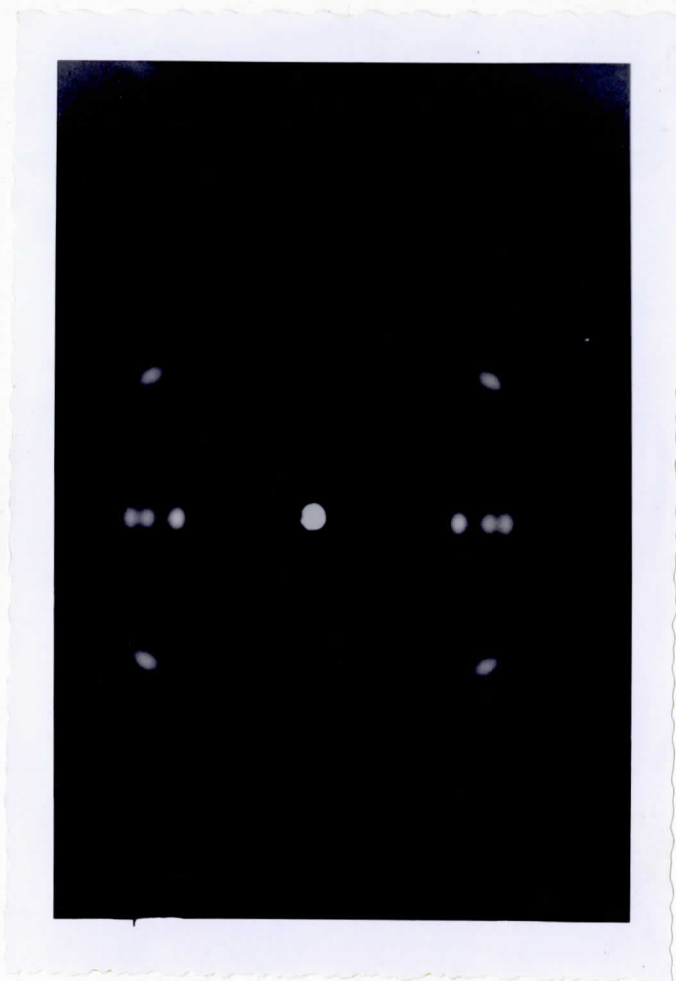


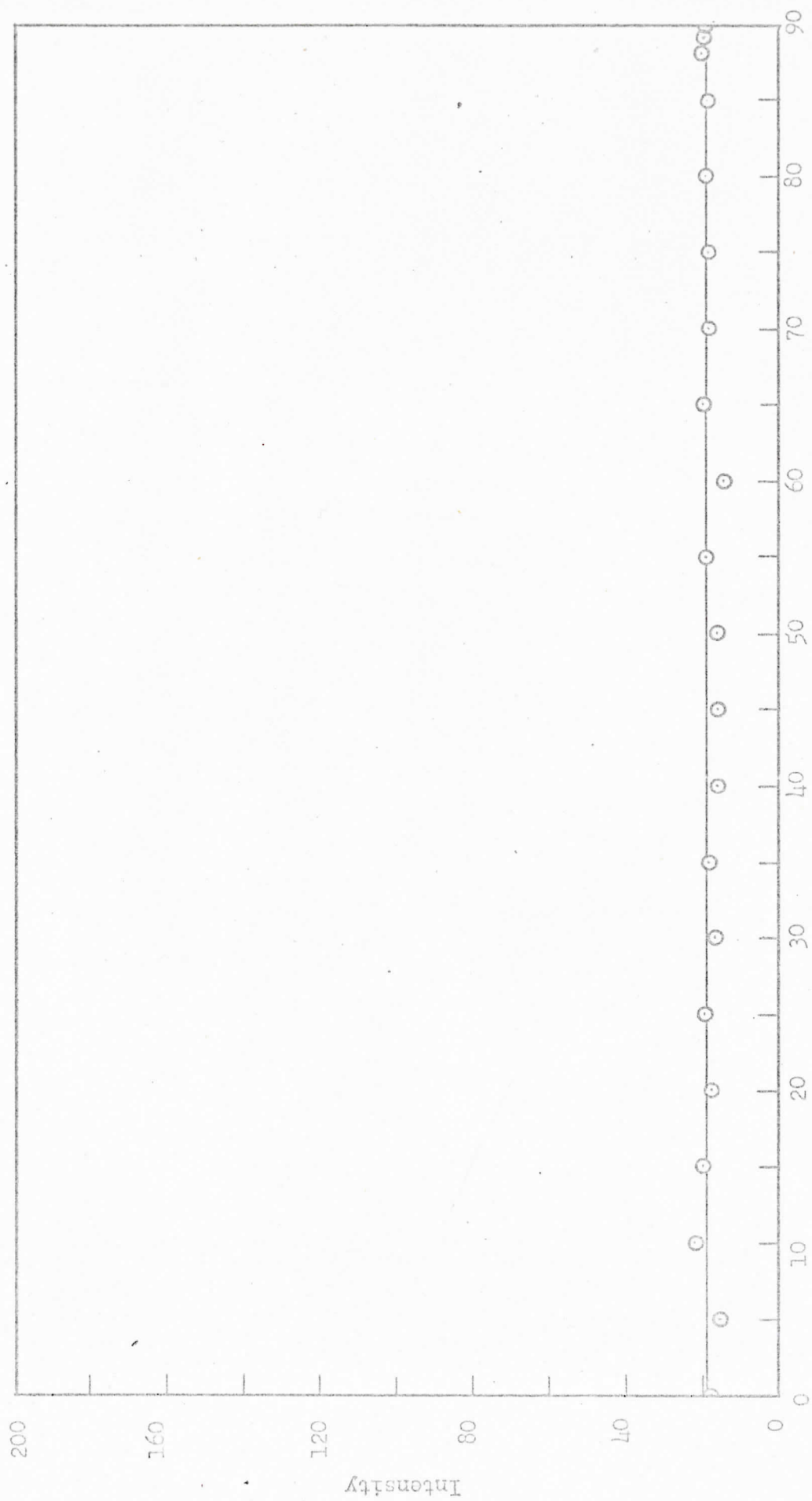
FIGURE 4

FLAT-PLATE X-RAY DIFFRACTION PATTERN OF A STEREOREGULAR  
POLYPROPYLENE FILM--DRAW RATIO 7.66

TABLE II

DIFFRACTED INTENSITIES AND AZIMUTHAL ANGLES OF  
SELECTED STEREOREGULAR POLYPROPYLENE FILMS

Angle, degrees	Intensity, arbitrary units		
	Sample 4, draw ratio of 1.00	Sample 7, draw ratio of 3.50	Sample 10, draw ratio of 7.66
0	118.0	91.0	25.7
10	121.9	90.2	20.0
20	117.4	86.5	24.6
30	116.7	89.3	26.8
40	116.3	91.0	22.1
50	116.1	98.3	26.2
60	114.1	103.2	24.0
70	118.4	108.6	25.1
75	118.7	117.1	25.3
77	-	121.1	30.2
80	119.0	134.3	40.9
82	-	143.1	52.3
83	-	148.7	70.7
84	-	154.0	93.0
85	119.3	158.7	118.6
86	-	161.9	145.0
87	-	165.5	163.4
88	120.8	166.9	172.4
89	119.7	167.7	176.6
90	120.2	168.1	177.7



Angle, Degrees

FIGURE 5

DIFFRACTED INTENSITY VERSUS AZIMUTHAL ANGLE FOR A STEREOREGULAR  
POLYPROPYLENE FILM OF DRAW RATIO 1.00

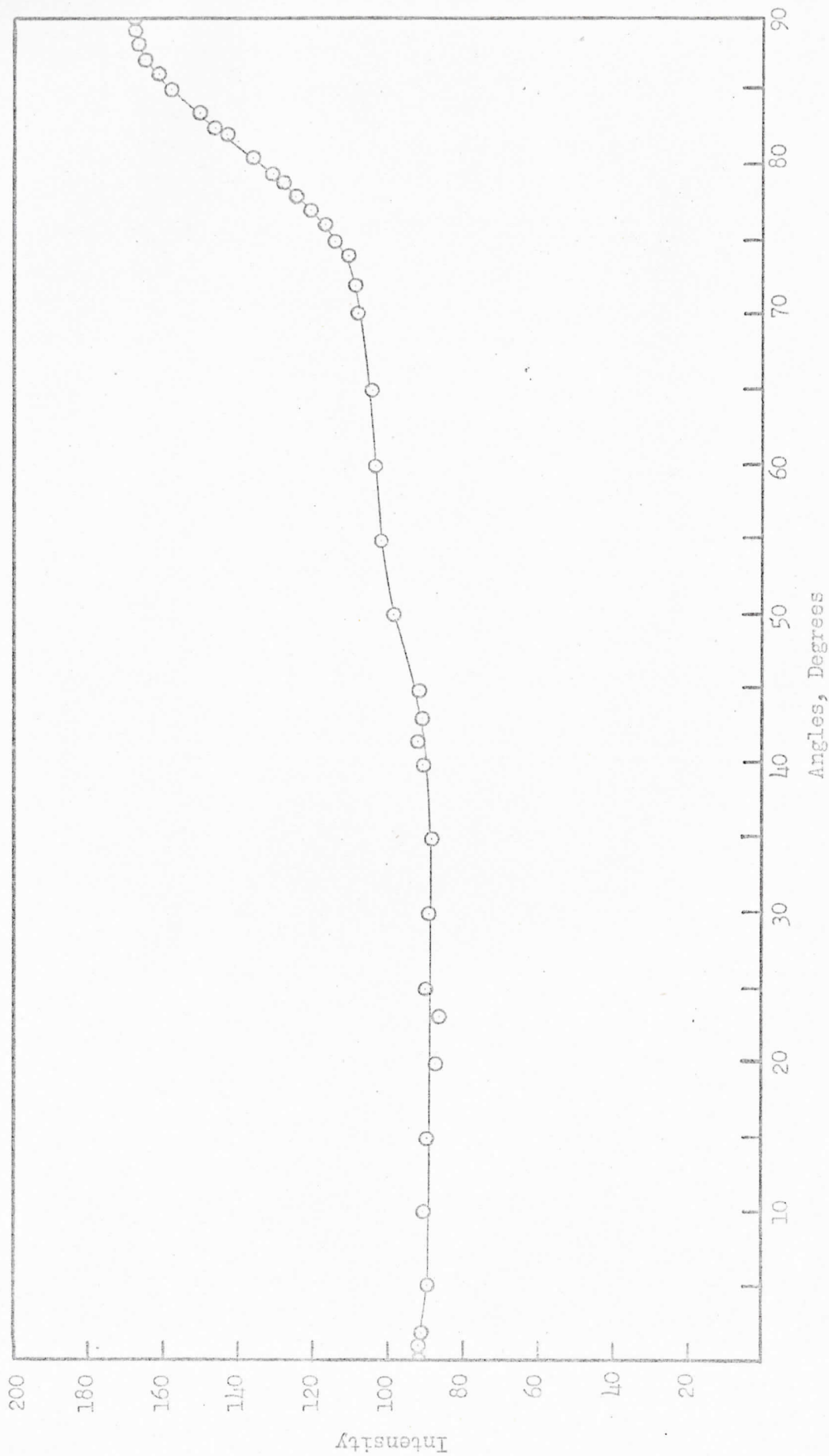


FIGURE 6  
 DIFFRACATED INTENSITY VERSUS AZIMUTHAL ANGLE FOR A STEREOREGULAR  
 POLYPROPYLENE FILM OF DRAW RATIO 3.50

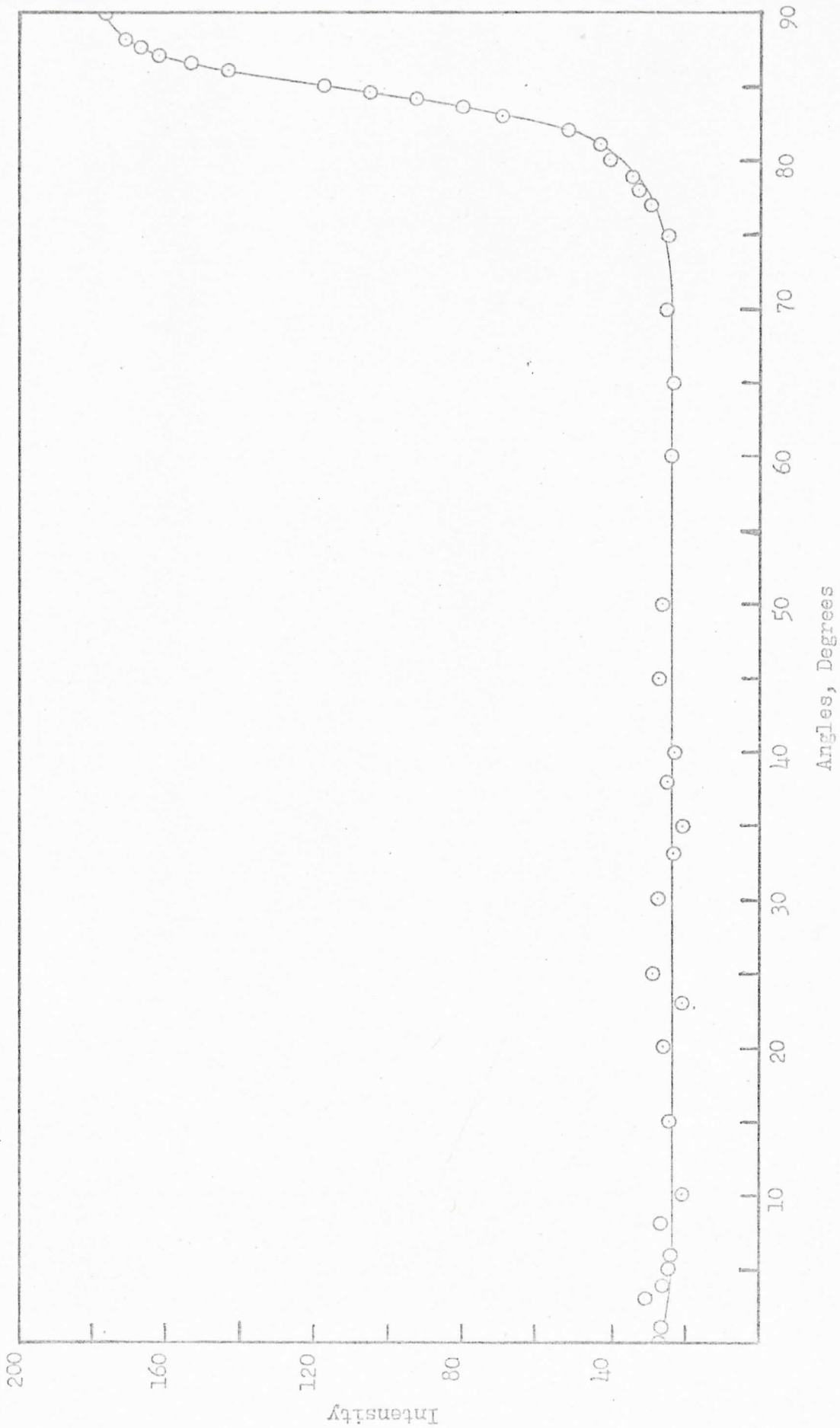


FIGURE 7

DIFFRACTED INTENSITY VERSUS AZIMUTHAL ANGLE FOR A STEREOREGULAR  
POLYPROPYLENE FILM OF DRAW RATIO 7.66



TABLE III

AVERAGE CRYSTALLITE ORIENTATION ANGLES AND DRAW RATIOS OF STEREOREGULAR POLYPROPYLENE FILMS

Sample	Draw ratio	Orientation angle, degrees
4	1.00	90.0
5	2.36	15.0
7	3.50	11.3
8	4.00	10.2
9	4.26	9.2
11	4.80	6.6
2	4.88	9.1
3	5.61	8.4
1	6.08	7.2
6	6.50	7.2
12	6.56	4.9
10	7.66	5.6

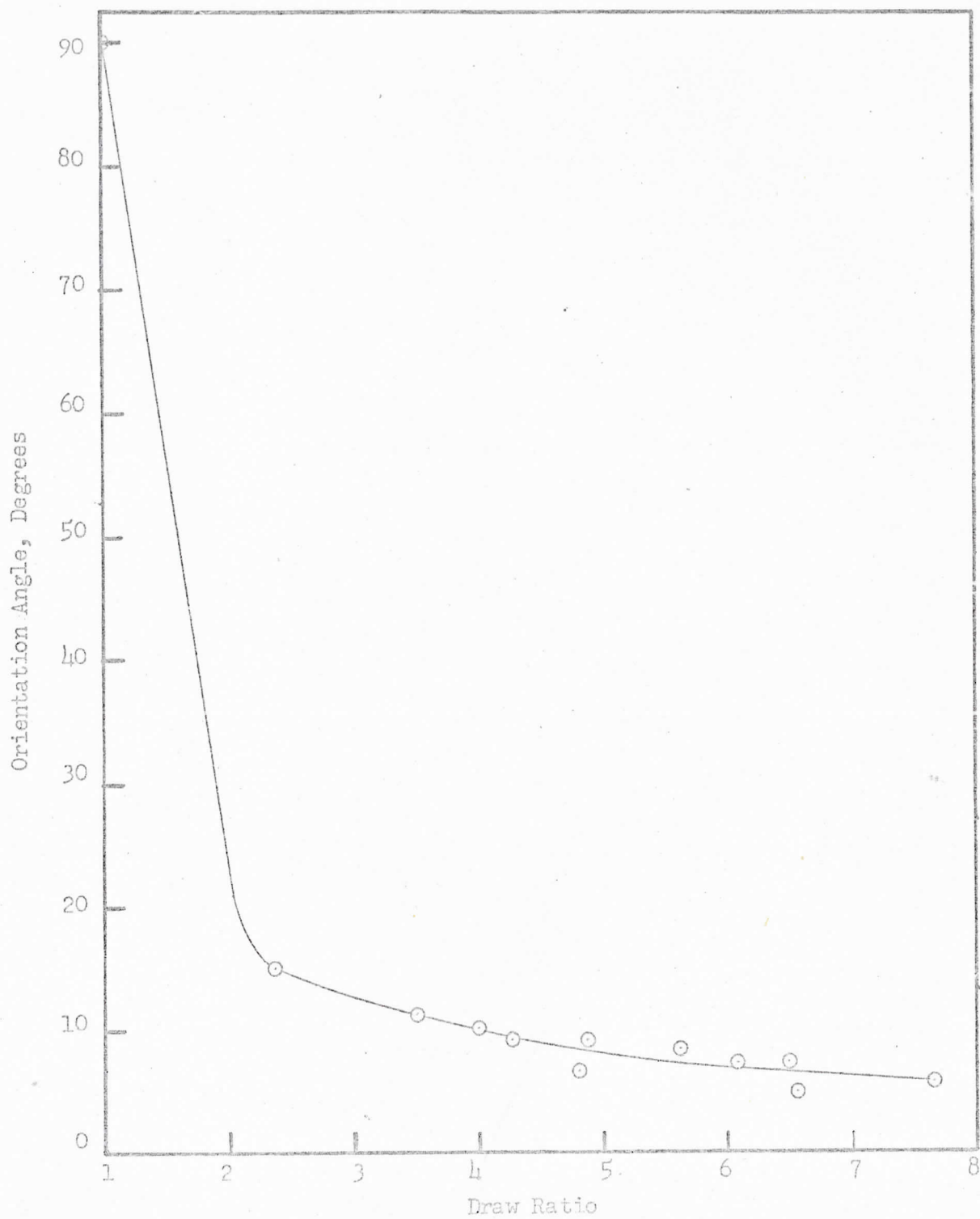
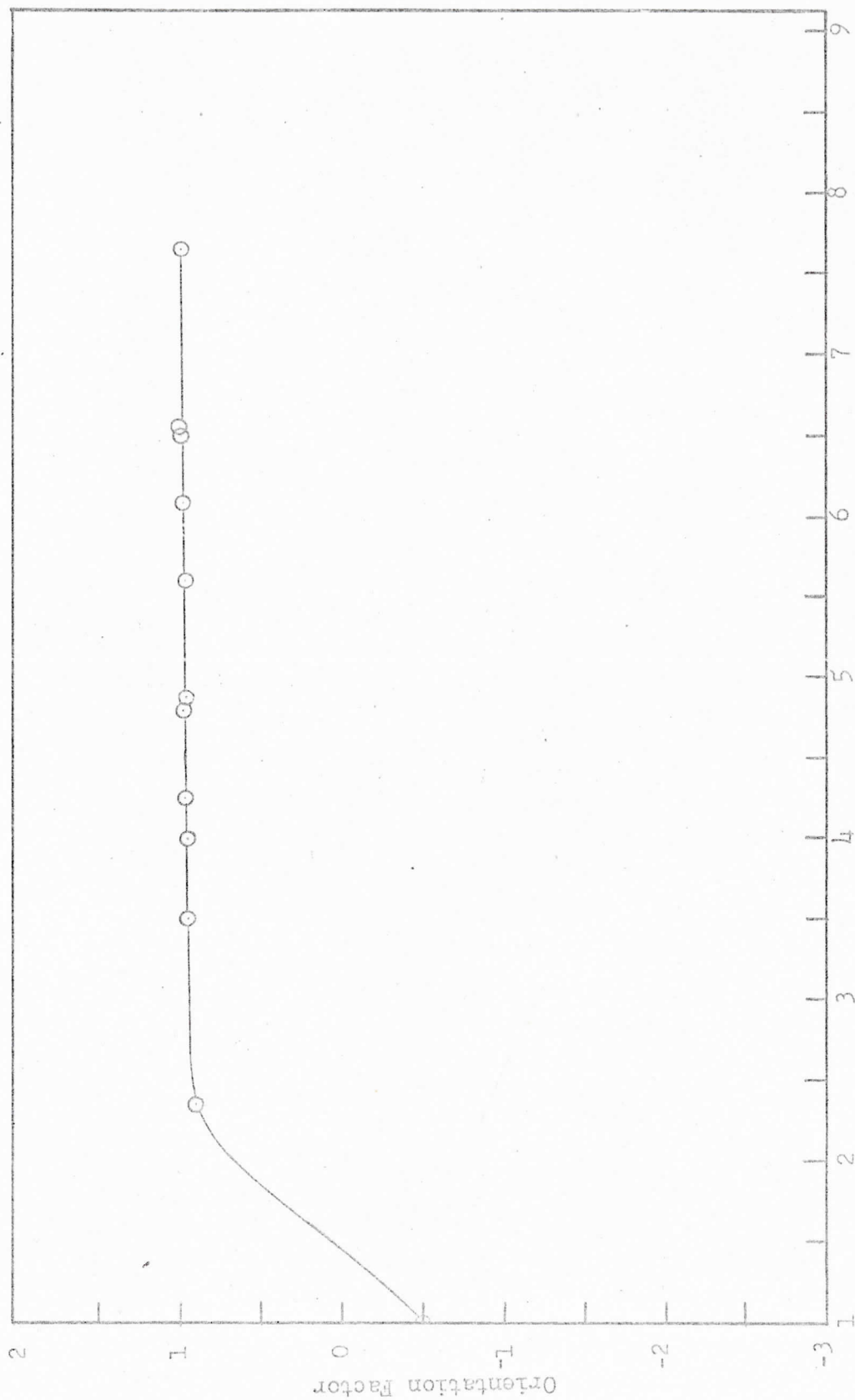


FIGURE 8

AVERAGE CRYSTALLITE ORIENTATION ANGLE VERSUS DRAW  
RATIO FOR STEREOREGULAR POLYPROPYLENE FILMS

TABLE IV  
 ORIENTATION FACTORS OF STEREOREGULAR  
 POLYPROPYLENE FILMS

Sample	Draw ratio	Orientation Factors		
		Total	Crystalline	Amorphous
4	1.00	-0.004	-0.500	0.324
5	2.36	-0.035	0.900	-1.413
7	3.50	0.089	0.942	-0.708
8	4.00	0.074	0.953	-0.854
9	4.26	0.085	0.962	-0.843
11	4.80	0.182	0.980	-0.604
2	4.88	0.216	0.962	-0.743
3	5.61	0.361	0.968	-0.449
1	6.08	0.370	0.976	-0.440
6	6.50	0.568	0.976	0.132
12	6.56	0.743	0.989	0.476
10	7.66	0.675	0.986	0.332



Draw Ratio

FIGURE 9

CRYSTALLITE ORIENTATION FACTOR VERSUS DRAW RATIO  
FOR STEREOREGULAR POLYPROPYLENE FILMS

## II. STUDIES OF DICHROISM WITH POLARIZED INFRARED RADIATION

Comparison of the absorption scans in Figures 10 and 11 indicates that drawn polypropylene films exhibit anisotropy with respect to the absorption of polarized infrared radiation. The absorbancies of each sample with the electric vector of the radiation first parallel to the draw axis and then perpendicular to the direction of draw are given in Table V along with the corresponding dichroic ratios. Table VI presents the total average angles of orientation calculated from the dichroic ratios of interest in this study is the fact that the anisotropy mentioned above becomes more pronounced at higher draw ratios. This trend is most apparent in Figure 12 where the total average orientation angle is observed to decrease as higher draw ratios are considered. Also worthy of note is the concave downward character of the curve, which indicates that early increments of draw are less effective in increasing orientation within the film than are later increments of equal size. The total orientation factors of the various films are listed in Table IV and plotted in Figure 13. In Figure 13 it can be seen that the total orientation factor makes no gain in the early stages of draw, even hinting at a decrease in value, but exhibits a relatively steady upward trend at draw ratios greater than 2.4. It should be noted that the relationship between the total orientation and the draw ratio demonstrated in these findings bears little similarity to the crystallite orientation versus extension observed by means of x-ray diffraction.

Wavelength In Microns

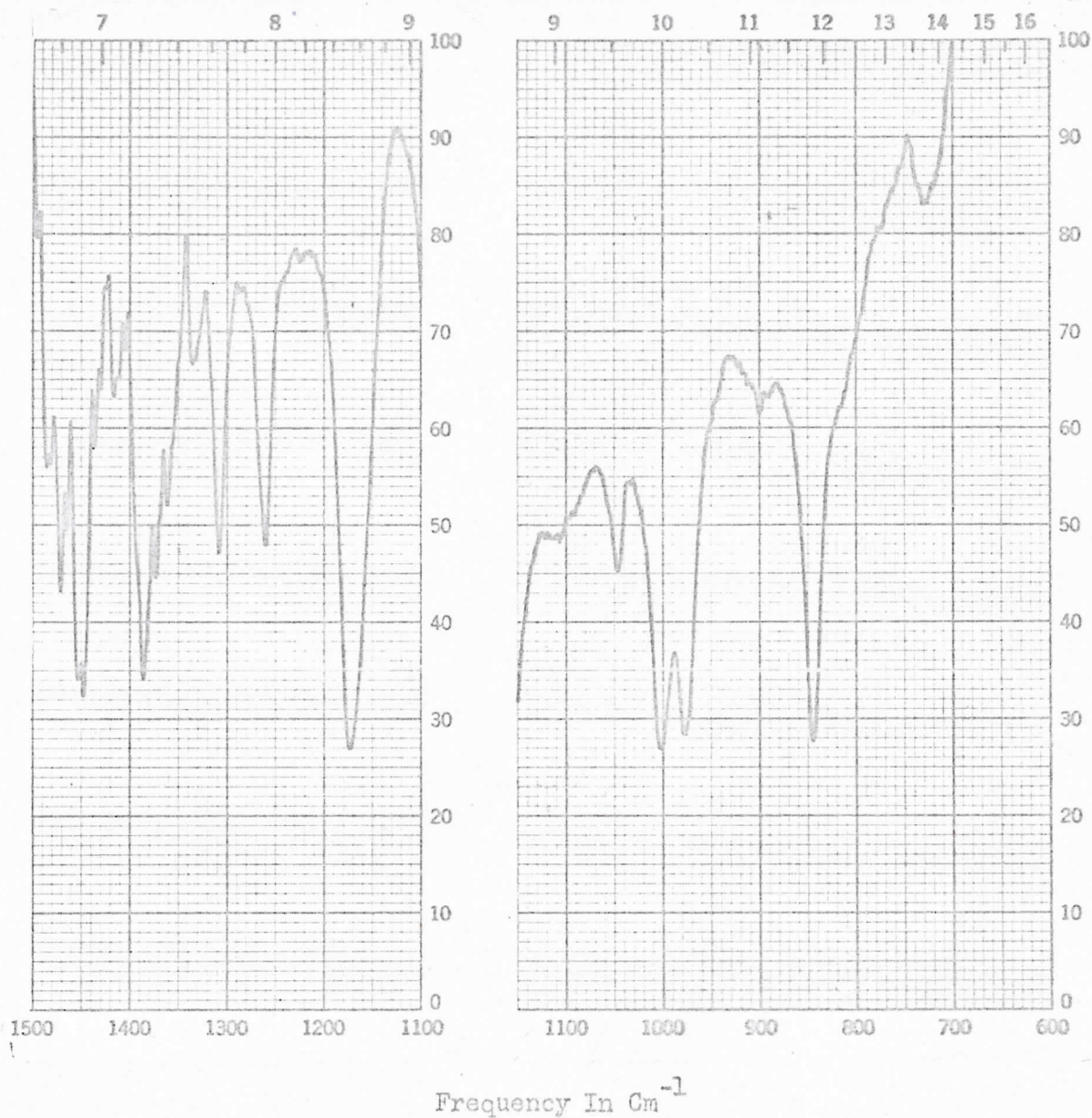
Frequency In  $\text{Cm}^{-1}$ 

FIGURE 10

PORTION OF THE POLARIZED INFRARED SPECTRUM OF A DRAWN  
 FILM OF STEREOREGULAR POLYPROPYLENE WITH THE DRAW  
 DIRECTION PARALLEL TO THE ELECTRIC VECTOR  
 OF THE POLARIZED RADIATION



Wavelength In Microns

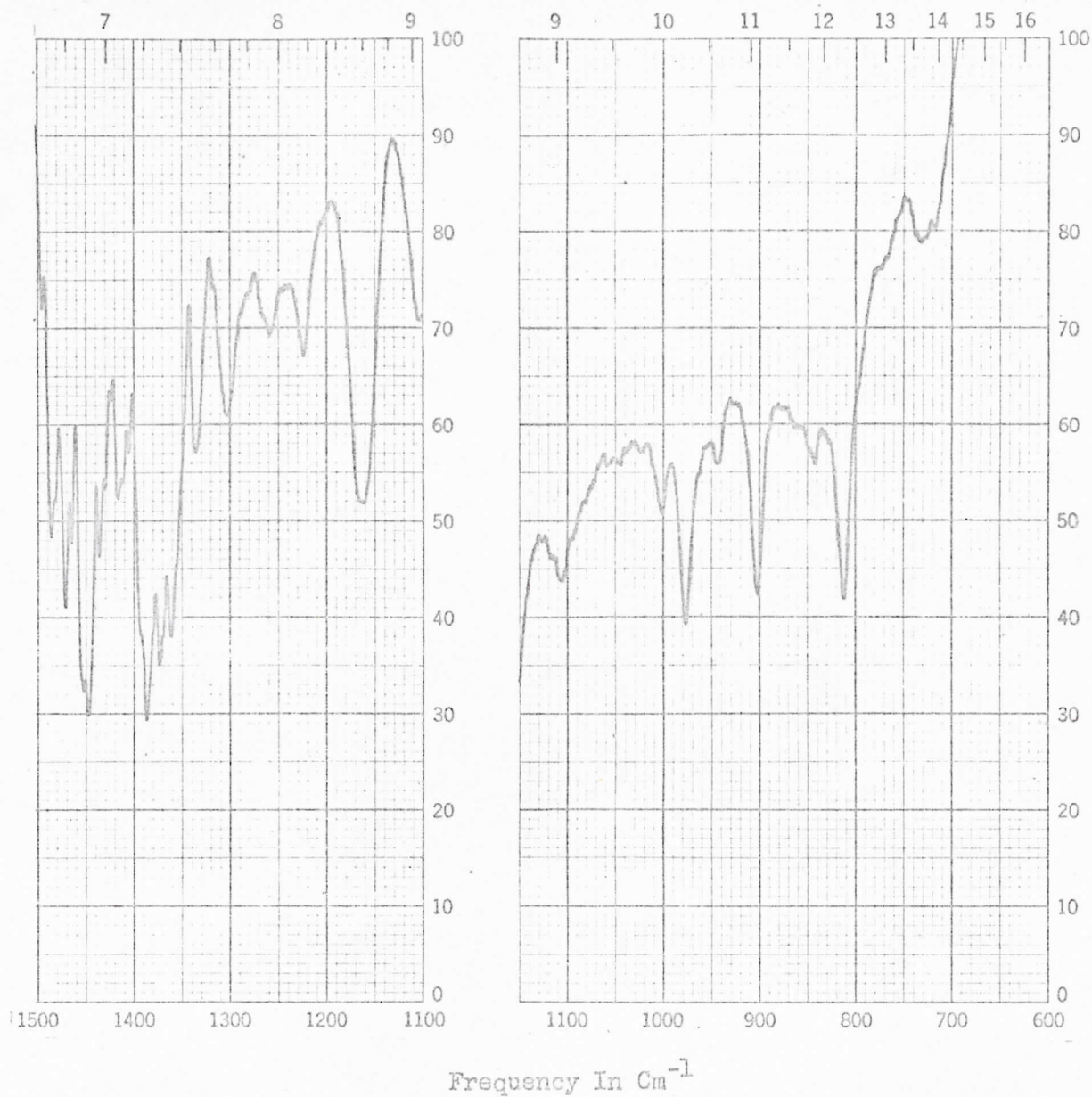


FIGURE 11

PORTION OF THE POLARIZED INFRARED SPECTRUM OF A DRAWN  
 FILM OF STEREOREGULAR POLYPROPYLENE WITH THE DRAW  
 DIRECTION PERPENDICULAR TO THE ELECTRIC  
 VECTOR OF THE POLARIZED RADIATION



TABLE V

ABSORBANCIES AND DICHROIC RATIOS OBSERVED IN THE INFRARED  
STUDIES OF STEREOREGULAR POLYPROPYLENE FILMS

Sample	Absorbance		Dichroic ratio
	Perpendicular	Parallel	
4	0.060	0.600	1.00
5	0.055	0.050	0.91
7	0.064	0.083	1.30
8	0.059	0.073	1.24
9	0.063	0.081	1.29
11	0.056	0.094	1.68
2	0.050	0.092	1.84
3	0.050	0.135	2.70
1	0.049	0.134	2.74
6	0.023	0.114	4.96
12	0.018	0.169	9.66
10	0.019	0.136	7.17

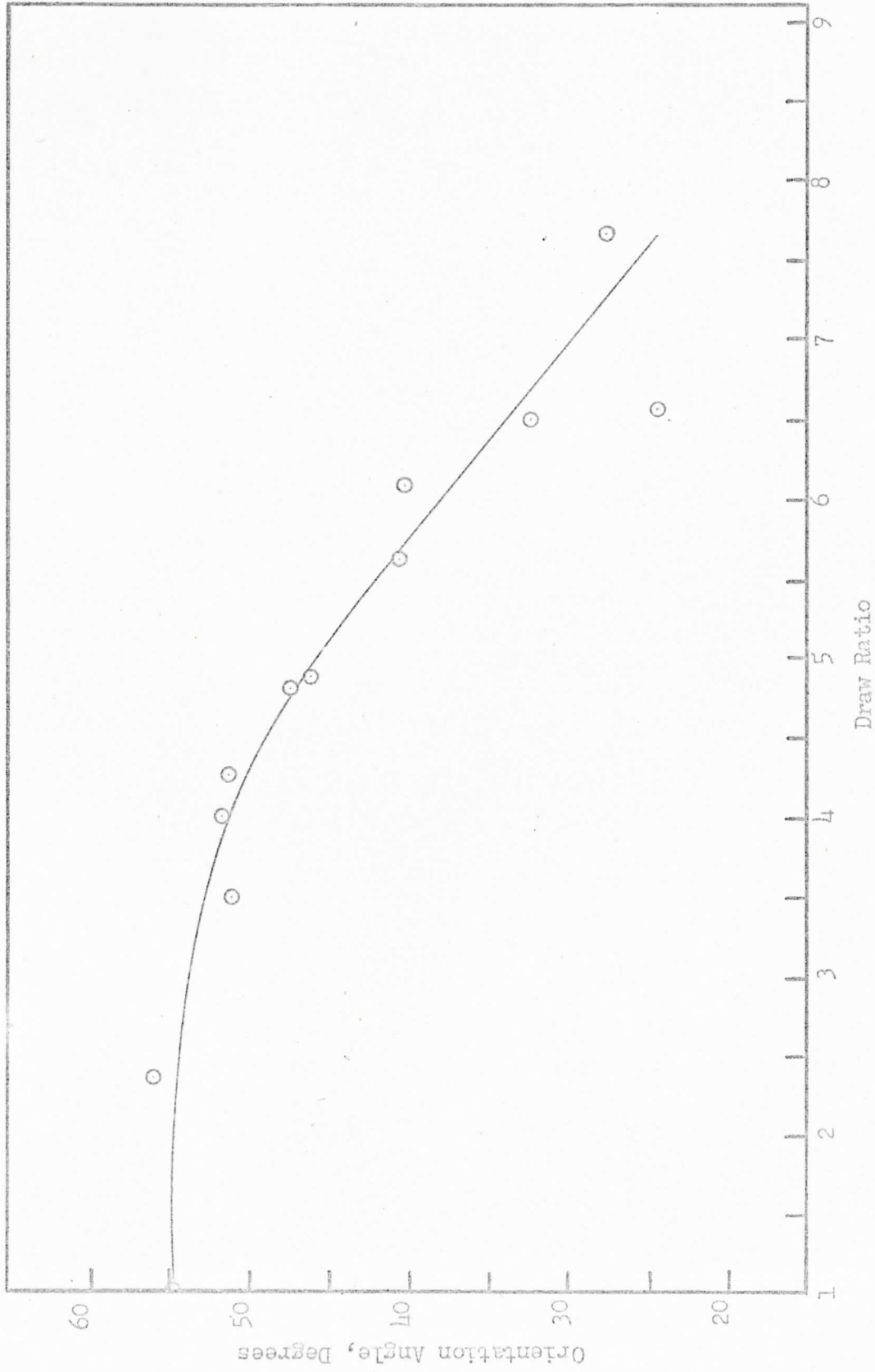


FIGURE 12  
TOTAL AVERAGE ORIENTATION ANGLE VERSUS DRAW  
RATIO FOR STEREOREGULAR POLYPROPYLENE FILMS

TABLE VI

TOTAL AVERAGE ORIENTATION ANGLES DICHROIC RATIOS, AND  
DRAW RATIOS OF STEREOREGULAR POLYPROPYLENE FILMS

Sample	Draw ratio	Orientation angle, degrees
4	1.00	54.8
5	2.36	56.0
7	3.50	51.2
8	4.00	51.8
9	4.26	51.3
11	4.80	47.5
2	4.88	46.2
3	5.61	40.7
1	6.08	40.3
6	6.50	32.4
12	6.56	24.5
10	7.66	27.8

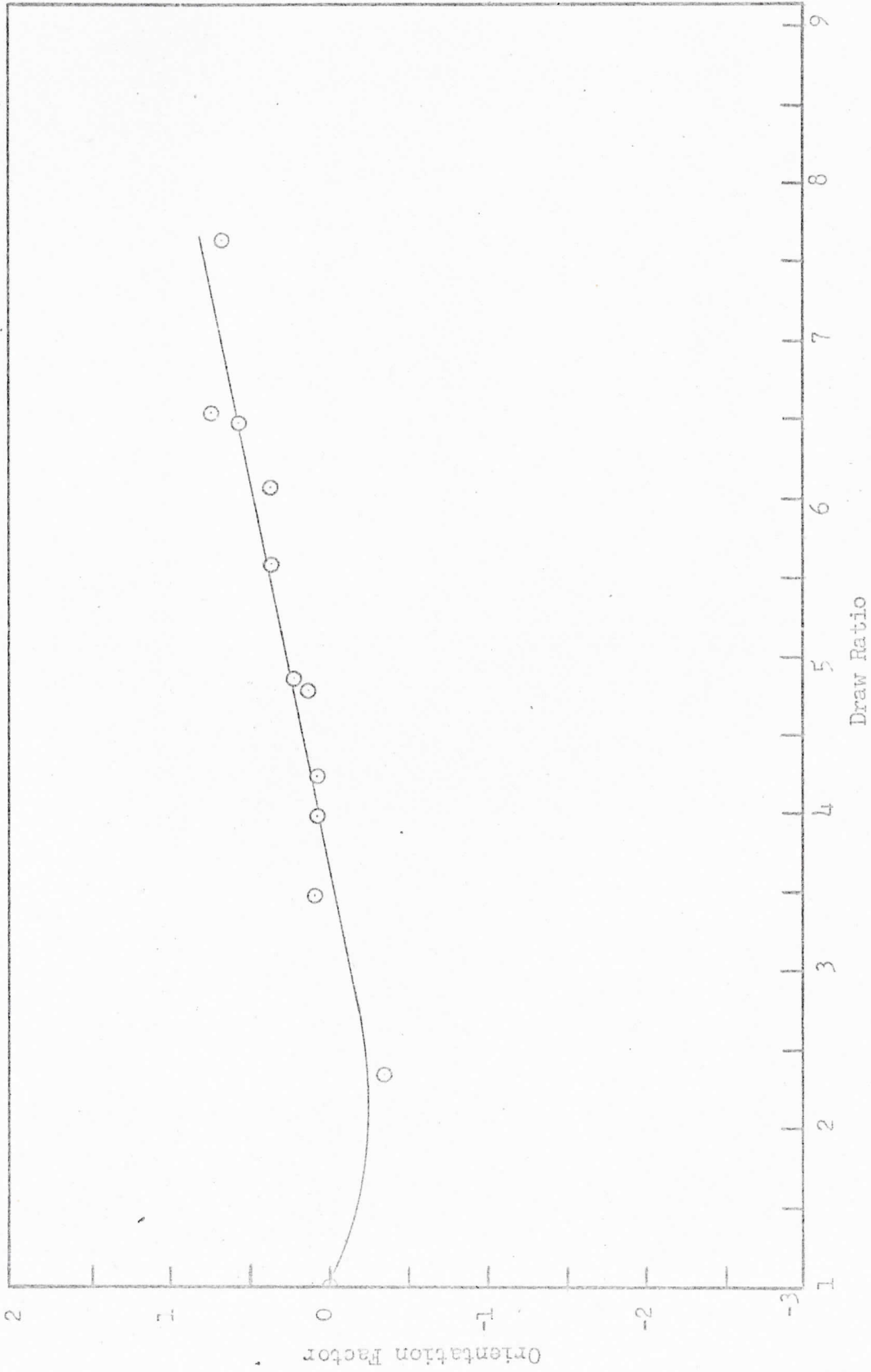


FIGURE 13  
TOTAL ORIENTATION FACTOR VERSUS DRAW RATIO  
FOR STEREOREGULAR POLYPROPYLENE FILMS

### III. DENSITIES AND PERCENTAGE CRYSTALLINITIES

The densities and percentage crystallinities of the polymer films are listed in Table VII. Figure 14, which contains a plot of percentage crystallinity versus draw ratio, indicates a poor correlation of the two parameters. A slight increase in crystallinity with increased draw is hinted, but it appears that variations in other factors such as the rate of cooling following the drawing process, the rate of draw, and the percentage crystallinity in the films prior to drawing may have obscured any significant correlations, if any, between extension and percentage crystallinity.

### IV. AMORPHOUS CONTRIBUTION TO ORIENTATION

It was stated earlier that the contribution of the amorphous regions to the total orientation could be evaluated from orientation angles obtained respectively from appropriate x-ray and infrared data provided the percentage crystallinity was known. For each sample, the amorphous orientation factors thus calculated are presented in Table IV.

The graph of amorphous orientation factors versus draw ratios, presented in Figure 15, reveals some interesting trends. During the early stages of draw the amorphous regions experienced a decrease in orientation reaching a minimum at a draw ratio of approximately 2.4. Beyond the minimum, amorphous orientation increased with increased extension.

Comparison of the orientation factors, crystallite total and amorphous, indicates that the increased orientation of crystallites at low

TABLE VII

PERCENTAGE CRYSTALLINITIES, DENSITIES, AND DRAW RATIOS OF STEREOREGULAR POLYPROPYLENE FILMS

Sample	Draw ratio	Density g/cm <sup>3</sup>	Percentage crystallinity
4	1.00	0.8861	39.78
5	2.36	0.9019	59.60
7	3.50	0.8928	48.30
8	4.00	0.8953	51.38
9	4.26	0.8953	51.38
11	4.80	0.8939	49.64
2	4.88	0.8991	56.17
3	5.61	0.9004	57.22
1	6.08	0.9004	57.22
6	6.50	0.8955	51.65
12	6.56	0.8957	51.92
10	7.66	0.8963	52.58

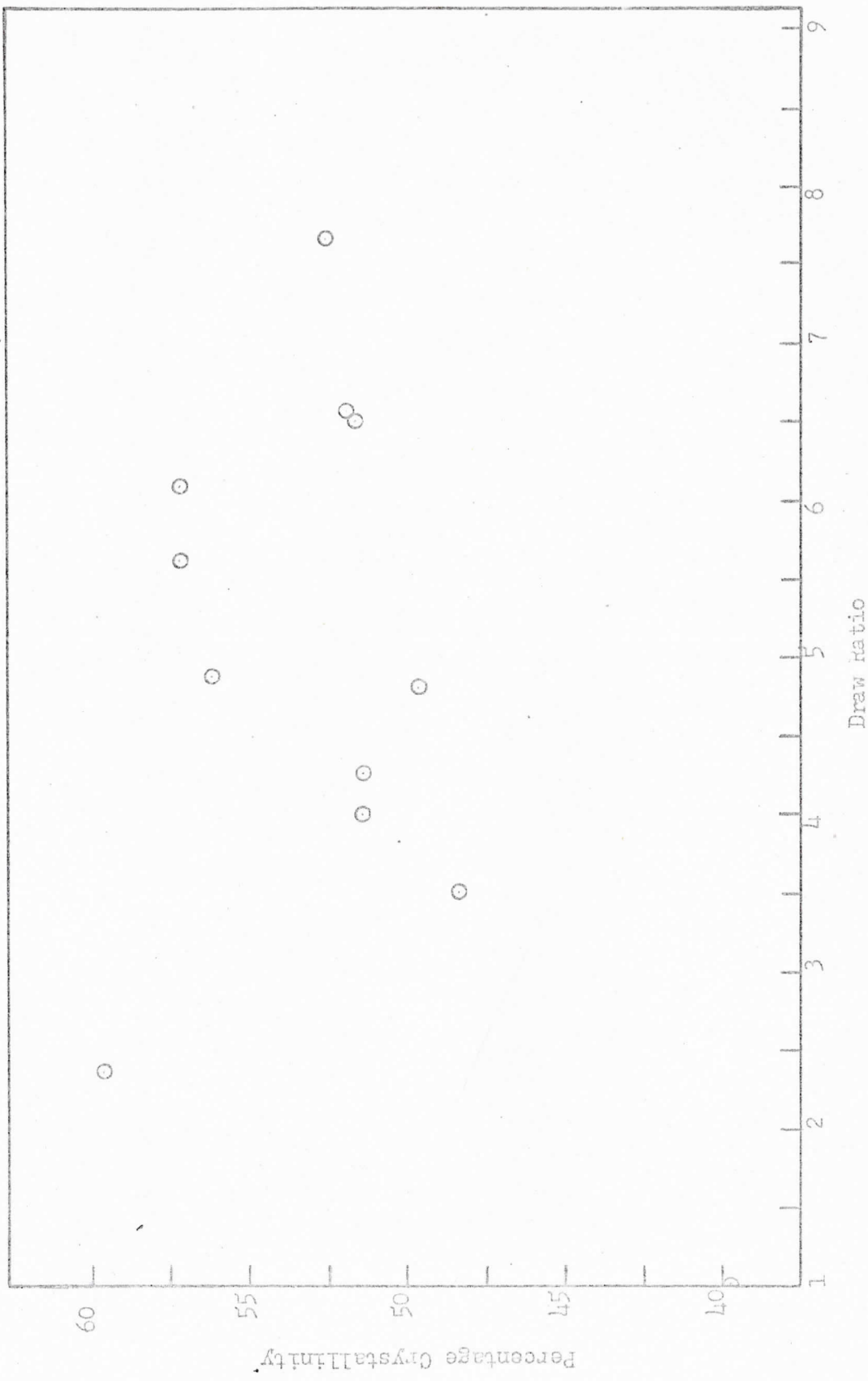
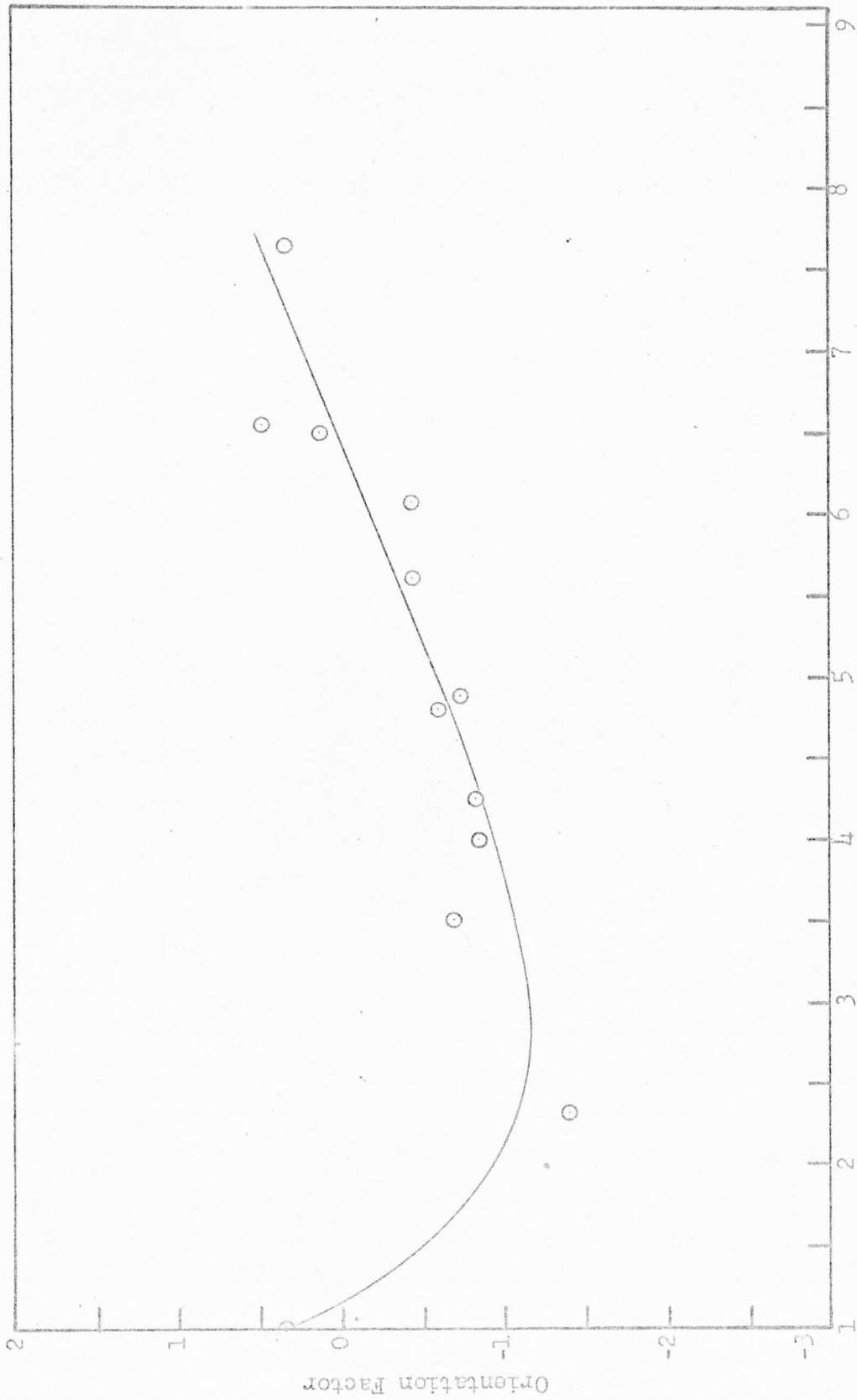


FIGURE 14  
 PERCENTAGE CRYSTALLINITY VERSUS DRAW RATIO  
 FOR STEREOREGULAR POLYPROPYLENE FILMS





AMORPHOUS ORIENTATION FACTOR VERSUS DRAW RATIO  
FOR STEREOREGULAR POLYPROPYLENE FILMS

FIGURE 15

draw is more than offset by an accompanying decreasing in orientation of the amorphous regions. However, beyond the draw ratio 2.4 the increased orientation of crystallites is negligible and the increased amorphous orientation is almost entirely responsible for the total orientation increase.

## CHAPTER V

### CONCLUSIONS

It was found in this investigation that the total orientation of drawn stereoregular polypropylene films could be divided into two distinct parts, the contribution from the crystallites and the amorphous contribution. Also observed, were two draw regions characterized by different orientation behavior: The low-draw region which extends from a draw ratio of unity to approximately 2.4, and a high-draw region extending from approximately 2.4 to the highest attainable draw ratios.

Crystallite orientation was observed to be extremely sensitive to film extension in the low-draw region reaching a nearly maximum value at draw ratio 2.4, followed by a slight upward trend in the high-draw region.

The amorphous portion of polypropylene, in contrast, exhibited a decrease in orientation in the low-draw region that slightly more than offset the orientation increase attributed to the crystallites. Throughout the high-draw region the noncrystalline orientation was found to increase with increased draw.

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