A STUDY OF THE INFRARED DICHROISM

IN

STEREOREGULAR POLYPROPYLENE

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A Thesis

Presented to

the Faculty of the Department of Chemistry

Appalachian State Teachers College

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In Partial Fulfillment

of the Requirements for the Degree

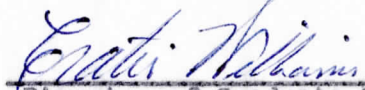Master of Arts

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by

Thomas Pinkney Murray

May, 1966

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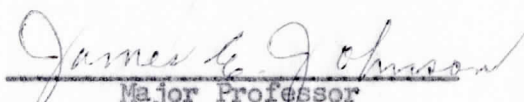
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STEREOREGULAR POLYPROPYLENE

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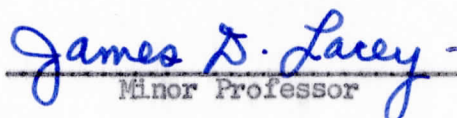
Thomas Pinkney Murray

Approved by:

H. G. Sink
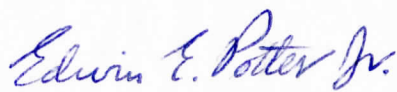Chairman, Advisory Committee

Cratis Williams
Director of Graduate Study

James G. Johnson
Major Professor

James D. Lacey — _Edwin E. Potter Jr._
Minor Professor

ACKNOWLEDGEMENT

To my parents.

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CHAPTER I

INTRODUCTION AND THE PROBLEM

I. INTRODUCTION

Stereoregular polypropylene, a synthetic polymer, is import-
ant for molded articles and textile fibers. Its industrial importance
has steadily increased since the discovery of its preparation in the
mid-fifties. To improve its physical and mechanical properties an under-
standing of its molecular structure is necessary, for it is well known
that these properties are closely related to the crystalline order and
orientation of the polymer molecules.

II. THE PROBLEM

Statement of the problem. This study was undertaken to pre-
pare appropriate polypropylene films of various degrees of extension,
to obtain densities and infrared dichroic ratios, to correlate draw ratio,
density, and dichroic ratios, and, finally, to draw conclusions about
the nature of the molecular orientation within the polypropylene films.

Importance of the problem. After-thermal (quenching and
annealing) and mechanical (pressing and drawing) treatments are employed
in the industrial processes of the fabrication of molded articles and
textile fibers. Such treatments are designed to produce desirable physi-
cal properties, and find their explanation in changes in the molecular

structure of the polymer. An understanding of the order and orientation structural parameters is of prime importance, therefore.

CHAPTER II

LITERATURE REVIEW

I. PREPARATION OF STEREOREGULAR POLYPROPYLENE

Stereoregular polypropylene is prepared by the polymeriza-
tion of propene with a Zeigler type stereospecific catalyst, obtained
by the interaction of aluminum alkyls and salts of Group IV and VI
metals (13)(16). Propene polymerizes by a free radical mechanism, in
a head to tail polymerization involving initiation, propagation and
termination (17). The reaction steps are shown in Figure I.

II. THE PHYSICAL STRUCTURE OF POLYPROPYLENE

Stereoregular polypropylene has the conventional two phase
order-disorder physical structure. The ordered (crystalline) regions
have the chain molecules aligned into a three dimensional lattice arrange-
ment. The disordered (amorphous) regions are areas of little or no
alignment (22). This order-disorder structure is a direct result of the
nature of the particular type of chain molecule and the type of inter-
molecular forces of attraction between the molecules. It is important,
therefore, to understand the nature of the chain configuration and
conformation.

The configuration of polymers may be atactic (5), syndiotactic
(6) or isotactic (13). These terms characterize the configuration of

FIGURE 1

THE POLYMERIZATION OF PROPENE TO POLYPROPYLENE

A. <u>Initiation</u> <u>Reaction</u>

$$R-R \longrightarrow 2R\cdot$$

$$R\cdot + CH_2=CH(CH_3) \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot$$

B. <u>Propagation</u> <u>Reaction</u>

$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} + CH_2=CH(CH_3) \longrightarrow R-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot$$

$$R-\left(CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}\right)_x-CH_2-\overset{}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot$$

C. <u>Termination</u> <u>Reaction</u>

$$R-\left(CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}\right)_x-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\cdot \quad \cdot\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\left(\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2\right)_x-R$$

$$R-CH_2-\left(\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2\right)_x-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\left(\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2\right)_x-R$$
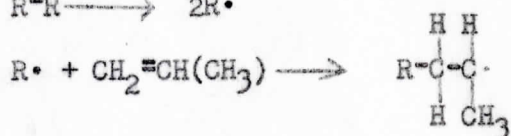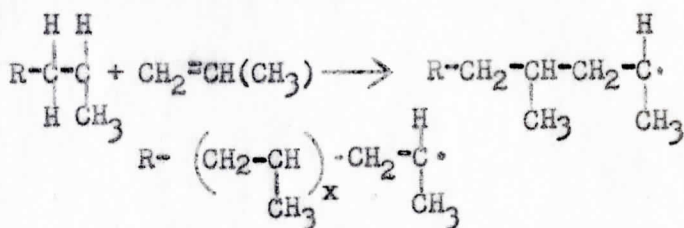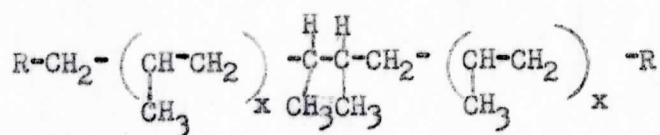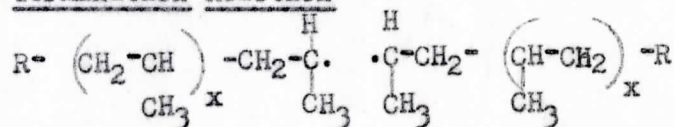
the polymer with respect to the positions of the functional groups attached to the backbone carbon chain. These configurations for polypropylene are illustrated in Figure 2. In a given polymer of polypropylene the relative amounts of the three configurations are fixed by the polymerization reaction, and are altered only by changing the polymerization reaction (18).

Chain conformations of polymers are planar, helical, twisted, or distorted. In stereoregular polypropylene, as with many vinyl polymers, the chain conformation is helical (3).

The interpretation of the physical properties of polymers involve the investigation of the changes in the order-disorder structure. Thus, in the drawing of polymer films or fibers the ordered regions are aligned parallel to the direction of extension. In addition, disordered regions are partially aligned so that there may be an augmentation of ordered regions and a decrease in disordered regions. This, therefore, produces an increase in the crystallinity and an orientation of the crystalline and amorphous regions. In addition to these effects, certain thermal and mechanical treatments may bring about alterations in the nature of the crystalline regions. A new crystalline structure has been reported for polypropylene (20)(21). Sobue and Tabata found the ordinary and quasi-crystalline structure was also found in low density-low draw ratio films. These investigations also found a reversal to the ordinary crystalline form with high orientation along the fiber axis when this film was stretched at $80^\circ - 150^\circ$C. These workers showed that annealing the film at 150°C for 15 minutes led to the irreversible transformation of the quasi-crystalline to the ordinary structure (20).

FIGURE 2

TACTICITY IN POLYPROPYLENE

A. <u>Isotactic</u>
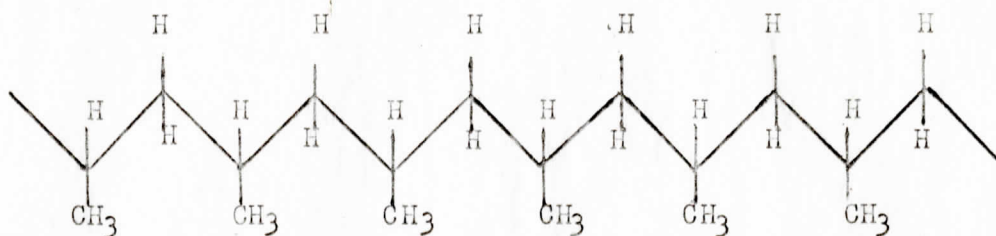
B. <u>Atactic</u>
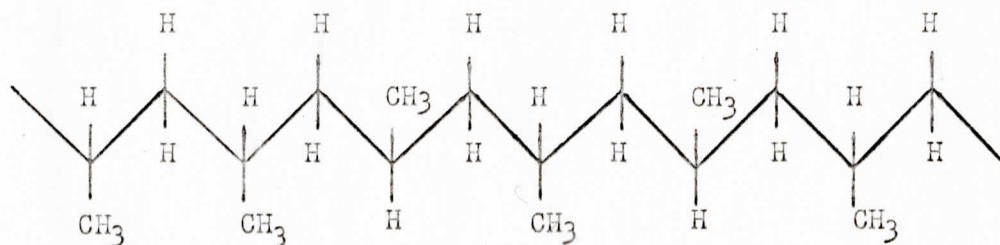
C. <u>Syndiotactic</u>
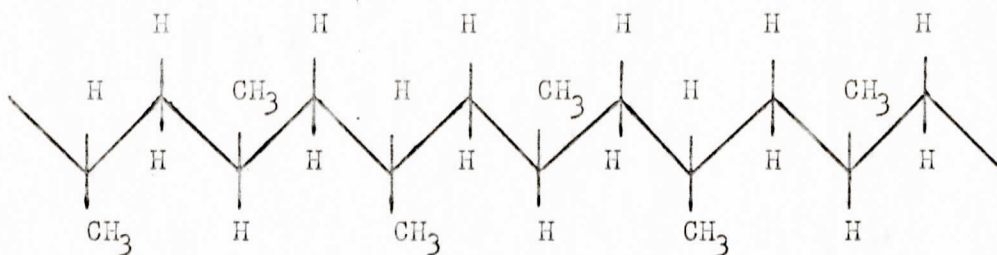
III. INFRARED BAND ASSIGNMENTS AND SYMMETRY

Many infrared studies (1)(6)(8)(9)(10)(11)(12)(14)(15)(19) have been made on stereoregular polypropylene because of the striking crystallinity effects(22). These have consisted of the use of un-polarized and polarized infrared radiation. Of these studies, the most useful for obtaining structural information with respect to the molecular orientation have been those which employed polarized radiation.

Polarized infrared spectra are usually obtained by using a polarizing element in association with the infrared spectrophotometer. Various types of polarizers are employed, but the most common is the one consisting of about six polished silver chloride plates placed with respect to the beam at the Brewster angle, α defined by

$$\tan \alpha = n$$

where n is the index of refraction of silver chloride (4)(22). Spectra of oriented films are obtained by first placing the fiber axis of the film parallel to the electric vector of the plane polarized radiation and then placing the fiber axis perpendicular to the electric vector. Absorbancies at different wavelengths are then obtained by a base line method described by Brugel (2) for the parallel and perpendicular posi-tions. The orientation of the absorption band is then defined in terms of the dichroic ratio, D.R. which is related to the absorbancy ratio by the following equation:

$$D.R. = \frac{A_\perp}{A_{||}}$$

where $A_\perp$ and $A_{||}$ are the absorbancies in perpendicular and parallel positions, respectively (22). For D.R. values less than 1.0, the absorption

band is called a parallel band, and for D.R. values greater than 1.0, the band is called a perpendicular band (22). As a result of such studies, Liang and Pearson (10) indexed the absorption bands, with respect to frequency, relative intensity (R.I.), polarization symmetry, and band assignments for stereoregular polypropylene. These are listed in Table I.

In other orientation studies by x-ray diffraction, Sabue and Tabata (20) examined stretched polypropylene filaments, and found that at draw ratios from 4 to 5, complete overall crystallite orientation parallel to the drawing direction was achieved. Schmidt (18), from infrared studies, considers that the maximum orientation is obtained only at maximum draw ratio. In this study, Schmidt found that the 840 cm^{-1} band to give the highest dichroic ratio while the 940 cm^{-1} band showed no dichroism.

Dichroic ratios are structural parameters which give a measure of the degree of the total molecular orientation of the chain molecules with respect to the direction of extension of the polymer film or fiber. A number of methods have been proposed for relating the average angle of orientation, θ, (the angle which the chain molecule makes with the fiber axis) and the infrared dichroic ratio. Each of these are special cases which apply to the particular type of oriented structure produced. In this particular study, it is assumed that an uniaxially oriented structure was produced by the stretching method. On the basis of this structure, the equation

$$\theta = \tan^{-1} \sqrt{2D.R.}$$

was derived (7). This deriviation is presented in a later section.

TABLE I

THE INFRARED SPECTRUM OF CRYSTALLINE POLYPROPYLENE (10)

Frequency cm^{-1}	R.I.	Polarization	Interpretation
805	w	⊥	
840	m	∥	
898	w	⊥	
940	vw	⊥	CH_2 rocking, C-C
972	m	∥	stretching and
995	m	∥	CH_3 wagging and
1044	vw	∥	rocking modes
1100	w	⊥	
1152	sh	⊥	
1165	m	∥	
1218	vw	⊥	
1255	w	∥	CH_2 twist and CH bend
1293	sh	⊥	
1303	w	∥	
1330	vw	⊥	CH_2 wagging and
1360	m	⊥	CH bend
1380	s	⊥	sym. CH_3 bending
1440	sh	⊥	
1455	s	∥	CH_2 bending and
1465	s	⊥	antisym. CH_3 bending
2836	s	∥	sy. CH_2 stretching
2866	s	⊥	
2875	s	⊥	sym. CH_3 stretch
2907	vs	∥	antisym. CH_2 stretch
2918	vs	⊥	CH stretching
2926	sh	—	
2947	vs	⊥	antisym. CH_3 stretch
2960	vs	∥	

In the processes of heating and orienting polymers it often happens that the crystallinity of the polymer will be changed. This is reflected in the density changes which occur. Sabue and Tabata (7)(8) measured the densities of various polypropylene films and fibers which had been stretched. Although the correlation between draw ratio and density was not good, the general trend was for the densities to increase with increasing draw ratio. The maximum density reached was about 0.90 (7) which was reached for a draw ratio between 4.0 and 5.0.

CHAPTER III

EXPERIMENTAL

I. MATERIALS AND EQUIPMENT

In this study Escon-125 stereoregular polypropylene in the
form of pellets from Enjay Chemical Company was used. Table II gives
the physical characterization of this sample.

The chemicals were Fisher technical grade xylene as a
polymer solvent, and carbon tetrachloride and toluene for density
gradient mixtures. Controlled temperature was maintained by use of a
Fisher thermoregulated water bath. In addition, a General Electric
250W. infrared heating lamp, a Model 20-1301, 2 Beuhler metallurgical
press with heating attachments were employed. A special stretching
frame was designed by the writer and built by the Walker Machine Company.
Figure 3 shows this frame. In addition, a microsample holder was
designed and built by the writer and Dr. W. C. Connolly of the Appalachian
State Teachers College Physics Department. Figure 4 shows the details
of the microsample holder. 3" x 3" glass plates and 3" x 4" Apollo
Ferrotype plates were used in the film casting processes. For the
calibration of the density bulbs used in the density gradient tube, a
Cenco Westphal balance was employed to measure densities. Finally, the
polarized infrared spectra were obtained with a Beckmann spectrophotometer,
IR-7, used in association with a beam condenser, silver chloride polarizer

TABLE II

PHYSICAL PROPERTIES OF ESCON-125 POLYPROPYLENE

GIVEN BY MANUFACTURER

PROPERTY	CONSTANT
Crystalline melting point	168°C.
Softening point	152°C.
Intrinsic viscosity	2.20
Flow rate	High
Coefficient of linear thermal expansion	6.46×10^{-5} in/in/$^{\circ}$C.
Specific heat at 73°F.	0.46 cal/g
Density at 73°F.	0.902
Weight average molecular weight	250,000
Burning rate	Slow
Water absorption	0.01%
Chemical resistance to acids	Good
Chemical resistance to alkalies	Excellent
Chemical resistance to organic solvents	Good
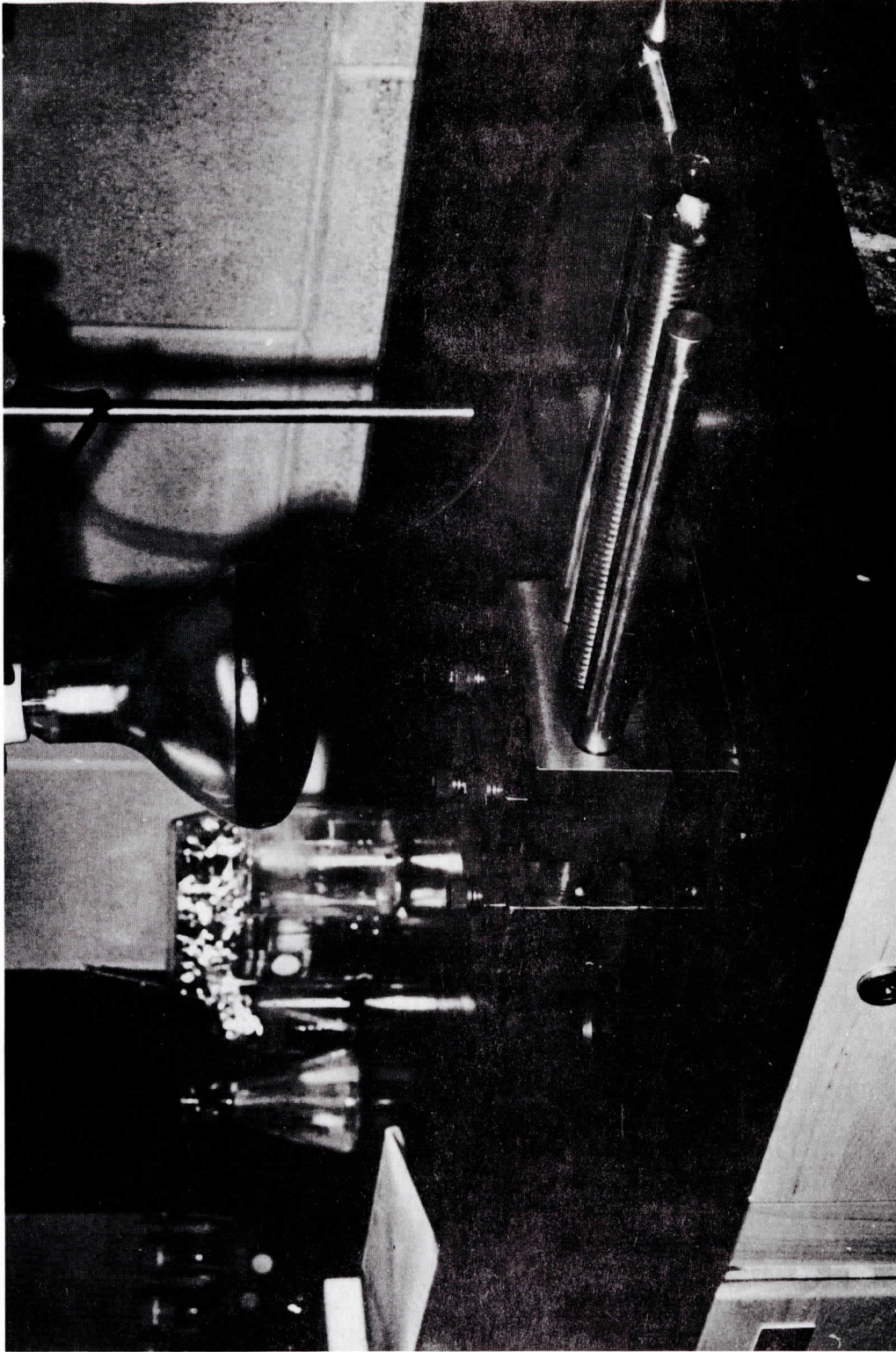
FIGURE 3

POLYMER STRETCHING FRAME
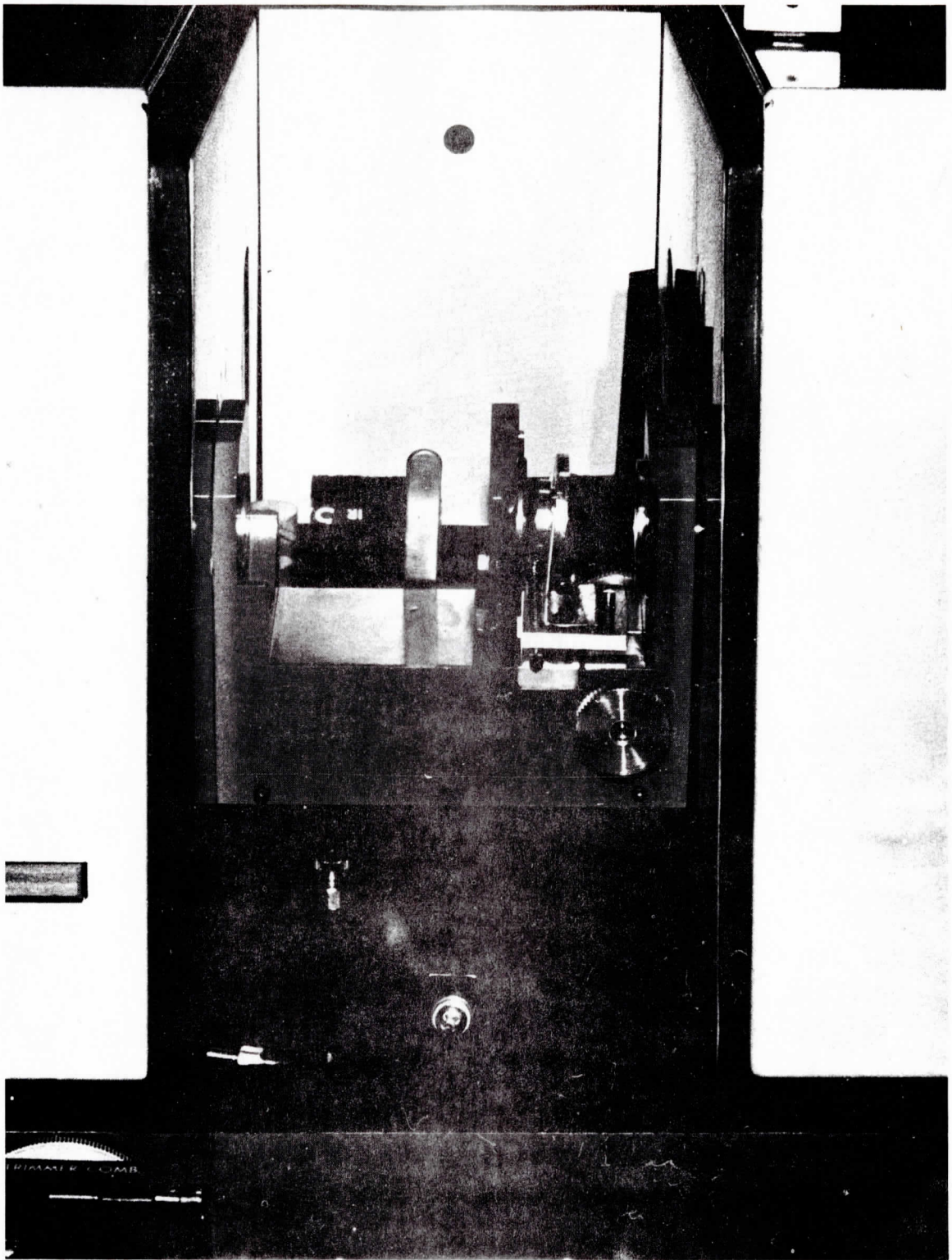
FIGURE 4

MICROSAMPLE HOLDER

and microsample holder by appropriate double beam operation.

II. METHOD

Preparation of polymer films. Three methods were investigated for preparing polypropylene films appropriate for drawing and infrared studies. In the first method, polymer was dissolved in xylene and poured on a hot glass plate. The solvent was then evaporated to leave a coherent polymer film which was then stripped from the plate. In this method the best concentration of polymer solution was about 0.5% by weight. In a second method, pellets were hot pressed with the Buehler press under various conditions of heating and time. Table III gives the conditions used. In a third method, a melt pressing technique was employed. In this method, chromium plated steel plates 3" x 4" were cut from an Apollo Ferrotype plate. 1.5 to 2.0 grams of polymer was sandwiched between the two plates, placed on a hot plate, and melted. Pressure was then applied to the upper plate to obtain a film of the desired thickness. The film was quenched in distilled water at 25°C. and stripped from the plate.

Drawing of the films. Films were drawn with the stretching frame previously described. The sample was clamped into the jaws of the instrument and stretched to the desired length by turning the hand crank. After extending the sample the jaws were loosened and the sample was removed. By means of a scale positioned parallel to the stretching direction, the draw ratio was determined and recorded. The draw ratio was then taken as the length after drawing minus the length before drawing divided by the length before drawing.

TABLE III

EXPERIMENTAL CONDITIONS USED TO PREPARE

FILM SAMPLES IN THE BUEHLER

PRESS

Sample	Heating time	Cooling time	Pressure	Thickness	Quality
B-1	5 min.	3 min.	4200 psi	0.040 cm.	poor
B-2	4	4	4200	0.065	good
B-3	4	4	4200	0.090	good
B-4	4	4	4200	0.070	good
B-5	4	4	4200	0.040	good
B-6	4	4	4200	0.050	good
B-7	4	4	4200	0.110	good
B-8	9	4	4200	0.140	poor
B-9	4	4	4200	0.140	good
B-10	4	4	4200	0.110	good
B-11	4	4	4200	0.110	good
B-12	5	6	4200	0.115	fair
B-13	5	4	4200	0.130	good
B-14	5	5	4200	0.190	good
B-15	6	5	4200	0.140	good
B-16	5	5	4200	0.180	good
B-17	5	5	4200	0.220	good

Films were drawn without heating and also by heating. Two methods of heating were employed. In the first method an Eagle conical heating coil, three inches long with a maximum diameter of one and three-fourth inches was positioned above the sample. The sample was heated so as to soften the polymer. The approximate temperature was $80°-95°C$. and the drawing rate was about 50 cm. per minute. In the second method, a 250W. General Electric infrared heating lamp was placed above the sample. The drawing took place at a temperature between $130°-140°C$. at a drawing rate of about 50 cm. per minute. Tables IV and V give data concerning the samples drawn under these two heating conditions.

Density of films. Densities were determined by means of a linear density gradient tube. This involved the construction and calibration of a gradient tube and finally the measurement of the densities of films having different draw ratios.

A "stacking" method was used to construct the tube. In this method successively less dense solutions of carbon tetrachloride and toluene were added to a 1000 ml. graduated cylinder. The tube was inclined about $40°$ from the vertical and, mixtures were added dropwise through a separatory funnel. The more dense mixture was added first and the least dense last. The composition and order of addition of each mixture are given in Table VI. The filled tube was than carefully placed in a constant temperature bath at $30 \pm 0.1°C$. After the temperature of the tube was that of the bath, a glass rod with a triangular bend was passed slowly down and back up the tube to allow a controlled amount of mixing

TABLE IV

DATA CONCERNING POLYPROPYLENE SAMPLES DRAWN

AT A TEMPERATURE OF 80° - 95°C.

Sample	Before Drawing	Thickness After Drawing	Heating time	Draw Ratio
F-17	0.018 cm.	0.016 cm.	1.00 min.	0.15
F-44	0.027	0.019	1.00	0.30
F-19	0.027	0.018	1.00	0.45
F-22	0.020	0.013	1.00	0.60
F-23	0.020	0.011	1.00	0.75
F-28	0.032	0.010	1.00	1.25
F-33	0.032	0.012	2.00	2.00
F-41	0.037	0.015	2.00	2.25
F-39	0.039	0.010	2.00	2.75
F-38	0.038	0.016	2.00	3.00
F-36	0.037	0.012	2.00	3.25
F-37	0.038	0.018	3.00	3.50
F-34	0.045	0.013	3.00	4.00
F-35	0.043	0.016	3.00	4.75

TABLE V

DATA CONCERNING POLYPROPYLENE SAMPLES DRAWN

AT A TEMPERATURE OF 130° - 140°C.

Sample	Thickness		Heating Time	Draw Ratio
	Before Drawing	After Drawing		
F-5	0.017 cm.	0.015 cm.	6.0 min.	0.5
F-6	0.020	0.006	6.0	1.0
F-7	0.021	0.009	6.0	1.5
F-8	0.021	0.008	6.0	2.0
F-9	0.024	0.006	6.0	2.5
F-10	0.025	0.008	6.0	3.0
F-11	0.025	0.007	6.0	3.5
F-12	0.025	0.008	6.0	4.0

TABLE VI

COMPOSITION OF SOLUTIONS USED IN THE DENSITY

GRADIENT TUBE

| Solution | Order into Tube | Mixture | | Volume of Mixture Used in Tube |
		Volume CCl_4	Volume C_7H_8	
a	1st	20 ml.	100 ml.	50 ml.
b	2	19	100	50
c	3	18	100	50
d	4	17	100	50
e	5	16	100	50
f	6	15	100	50
g	7	14	100	50
h	8	13	100	50
i	9	12	100	50
j	10	11	100	50
k	11	10	100	50
l	12	9	100	50
m	13	8	100	50
n	14	7	100	50
o	15	6	100	50
p	16	5	100	50
q	17	4	100	50
r	18	3	100	50
s	19	2	100	50
t	20	1	100	50
u	21	0	100	50

of the various layers. The tube was allowed to stand undisturbed in the bath for twelve hours to equilibrate.

To calibrate the tube, densities of various glass bulbs were obtained by a flotation method. Densities of the equilibrating liquids were measured by means of a Westphal balance. These calibrated bulbs (Table VII) were placed in the gradient tube, and after equilibrum was reached, the cylinder readings were recorded. The cylinder readings were then plotted versus the corresponding densities to obtain the calibration curve.

The densities of the polymer films were determined by carefully placing the samples under the liquid surface, allowing them time to equilibrate, and then recording the cylinder position. By means of the calibration curve, the densities were obtained and recorded.

Infrared spectra of polymer samples. The infrared spectrum of an un-oriented film was obtained by programming into the instrument the appropriate conditions of slit program, gain, period and scanning speed for double beam operation. Figure 5 shows this spectrum.

The spectra for the oriented films were obtained by placing the beam condenser and polarizer in the sample beam. The sample mounted in the microsample holder was then placed at the focal point of the condensed beam. Spectra for each sample were recorded twice. One in which the electric vector of the polarized beam was parallel and also the electric vector was perpendicular to the direction of draw. The absorbancies of the various absorption bands were then determined for the parallel and perpendicular scans by the base line method. From these

TABLE VII

DENSITY OF GLASS BLUBS USED TO CALIBRATE
THE DENSITY GRADIENT TUBE

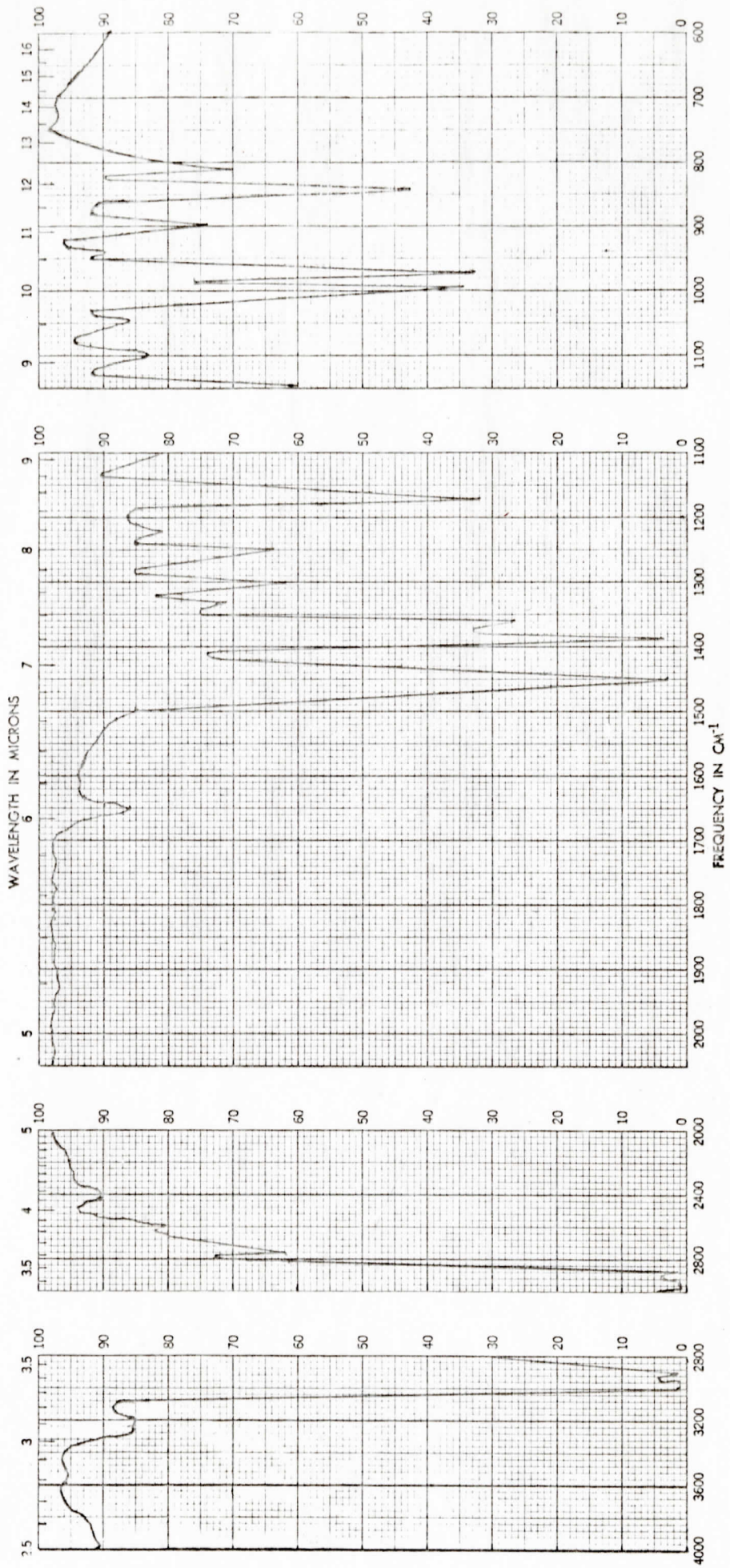| Bulb	Density @ 30.02°C.
#1	0.9691
#2	0.9678
#3	0.9266*
#4	0.9599*
#5	0.9399
#6	0.8723
#7	0.8744
#8	0.8653
#9	0.9978
#10	0.8865*
#11	0.9029*
#12	0.8923

*Used in the calibration of the gradient tube

FIGURE 5

THE INFRARED SPECTRUM OF AN UNORIENTED
POLYPROPYLENE SAMPLE

data the dichroic ratios for the various bands were calculated from the equation

$$D.R. = \frac{A\perp}{A_{||}}$$

In order to calculate the average orientation angle θ, it was necessary to derive the relationship between θ and the dichroic ratio, D.R. This has been carried out by J. E. Johnson (7) and is presented below.
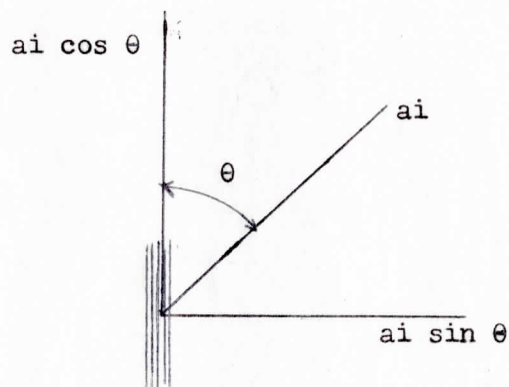
Assume that a molecule which shows dichroism is embedded in a polymer matrix. Assume also that the light which is vibrating parallel to the long axis of the molecule is absorbed and the light which is vibrating perpendicular to the long axis of the molecule is transmitted.

Suppose a beam of light is plane polarized at an angle θ. Its amplitude is ai.

The component of the light which is vibrating parallel to the long axis has an amplitude:

$$A_{||} = ai \cos \theta$$

The component of light vibrating perpendicular to the long axis will have an amplitude:

$$A_\perp = ai \sin \theta$$

after the light strikes the molecule, the component perpendicular to the molecule which is transmitted will have an amplitude:

$$A_\perp = ai \sin \theta$$

However, the amplitude of the parallel component will be reduced due to absorption to

$$A_\parallel = a \cos \theta$$

The intensity of the light will be

$$I = A^2$$

where A is the amplitude of the vibrating light.

The total intensity, I_T will give by

$$(A_\parallel)^2 + (A_\perp)^2$$

$$I_T = [a \cos \theta]^2 + [ai \sin \theta]^2$$

$$I_T = a^2 \cos^2 \theta + ai^2 \sin^2 \theta$$

Let g_0 be the fraction of the light transmitted which is vibrating parallel to the long axis of the molecule. Also, let g be the fraction of light which is vibrating at any other angle θ.

$$a^2 = g_0 \, ai^2$$

$$I_T = ai^2 \, g_0 \cos^2 \theta + ai^2 \sin^2 \theta$$

$$\frac{I_T}{ai^2} = g_0 \cos^2 \theta + \sin^2 \theta$$

$$g = \frac{I_T}{ai^2} \quad \text{or} \quad g = g_0 \cos^2 \theta + \sin^2 \theta$$

$$g = g_0 \cos^2 \theta + 1 - \cos^2 \theta$$

$$1-g = 1-(g_0 \cos^2 \theta + 1 - \cos^2 \theta)$$

$$1-g = 1-g_0 \cos^2 \theta - 1 - \cos^2 \theta$$

$$1-g = \cos^2 \theta (1-g_0)$$

$$g = e^{-kcb}$$

$$g_0 = e^{-(kcb)o}$$

$$1 - e^{-kcb} = \cos^2 \theta \; 1-e^{-(kcb)o}$$

$$e^{-x} = 1-x + \frac{x^2}{2!} - \frac{x^3}{3!} + \ldots$$

$$e^{-kcb} = 1-kcb + \frac{(kcb)^2}{2!} - \frac{(kcb)^3}{3!} + \ldots$$

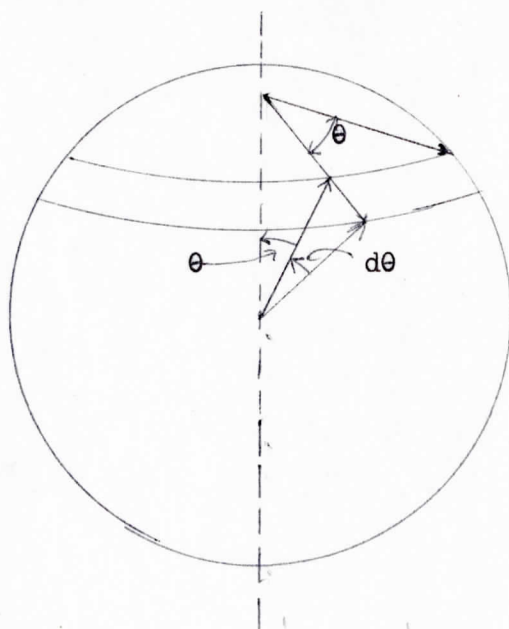$$1-e^{-kcb} = 1-1 + kcb - \frac{(kcb)^2}{2!} + \frac{(kcb)^3}{3!}$$

as a good approximation

$$1-e^{-kcb} = 1-g = kcb$$

and

$$1-g_0 = (kcb)o$$

When the above is multiplied by $\log_e$, we obtain the optical density for light vibrating in the direction θ.

In a fiber or uniaxially orientated film, the angular distribution of molecules around the fiber axis is represented by the intersection of the long axis with the pole sphere. If we treat the structure as a uniaxial one, the density distribution of the pole sphere intersections is a function of (θ) only.

For random orientation $f(\theta)$ is constant. Suppose we divide the pole sphere into zones each of which have an angular width of $d\theta$. The number of molecules in a zone is

$$n = 2\pi f(\theta)\sin\theta\, d\theta$$

$$N = 2\pi\int_{0}^{\pi} f(\theta)\sin\theta\, d\theta$$

The optical density for one molecule is given by

$$\log_e (kcb)_o \cos^2\theta$$

For n molecules the optical density is

$$\log_e (kcb)_o \cos^2\theta\, f(\theta) \times 2\pi\sin\theta\, d\theta$$

For N molecules, the total optical density for light vibrating parallel to the long axis of the molecule is:

$$D_{\shortparallel} = \log_e (kcb)_o \times 2\pi\int_{0}^{\pi} f(\theta)\sin\theta\cos^2\theta\, d\theta$$

$$D_{\shortparallel} = \log_e (kcb)_o \times 2\pi N\frac{\int_{0}^{\pi} f(\theta)\cos^2\theta\sin\theta\, d\theta}{N}$$

$$D_{\shortparallel} = \log_e (kCb)\frac{2\pi\int_{0}^{\pi} f(\theta)\cos^2\theta\sin\theta\, d\theta}{2\pi\int_{0}^{\pi} f(\theta)\sin\theta\, d\theta}$$

Here C is the total concentration of the N molecules

$$C = cN$$

$\log_e (kCb)_o$ = optical density if all the molecules are orientated with their long axis parallel to the direction of vibration of light.

Let $D_o = \log_e (kCb)_o$

The ratio of the integrals will be the average value of the $\cos^2 \theta$. Thus

$$\overline{\cos^2 \theta} = \frac{\int_0^{\pi} f(\theta) \cos^2 \theta \sin \theta \, d\theta}{\int_0^{\pi} f(\theta) \sin \theta \, d\theta}$$

Thus:

$$D_{||} = D_0 \overline{\cos^2 \theta}$$

Since the molecules are uniformly distributed about the fiber axis, the average optical density for light vibrating perpendicular to the fiber axis is given by:

$$\log_e (kCb)_0 \sin^2 \theta \frac{\int_0^{2\pi} \cos^2 \mathbb{D} \, d\mathbb{D}}{\int_0^{\pi} d\mathbb{D}} =$$

$$\tfrac{1}{2} \log_e (kCb)_0 \sin^2 \theta$$

Integrating for all the N molecules in the N zones.

$$D_{\perp} = \tfrac{1}{2} \log_e (kCb)_0 \times 2\pi \int_0^{\pi} f(\theta) \sin^2 \theta \, d\theta$$

$$D_{\perp} = \tfrac{1}{2} \log_e (kCb)_0 \times 2\pi N \frac{\int_0^{\pi} f(\theta) \sin^2 \theta \sin \theta \, d\theta}{N}$$

$$D_{\perp} = \tfrac{1}{2} \log_e (kCb)_0 \frac{2\pi \int_0^{\pi} f(\theta) \sin^2 \theta \sin \theta \, d\theta}{2\pi \int_0^{\pi} f(\theta) \sin \theta \, d\theta}$$

$$D_{\perp} = \tfrac{1}{2} D_0 \overline{\sin^2 \theta}$$

$$D_{||} + 2D_{\perp} = D_0 \overline{\cos^2 \theta} + 2\left[\tfrac{1}{2} D_0 \overline{\sin^2 \theta}\right]$$

$$D_{||} + 2D_{\perp} = D_0 (\cos^2 \theta + \sin^2 \theta)$$

$$D_{||} + 2D_{\perp} = D_0$$

$$\frac{D_{||} - D_{\perp}}{D_{||} + 2D_{\perp}} = \frac{D_0 \overline{\cos^2 \theta} - \tfrac{1}{2} D_0 \overline{\sin^2 \theta}}{D_0} = \overline{\cos^2 \theta} - \tfrac{1}{2}\overline{\sin^2 \theta}$$

$$\frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} = \overline{1 - \sin^2 \theta} - \tfrac{1}{2} \overline{\sin^2 \theta} = 1 - 3/2 \overline{\sin^2 \theta}$$

This defines the orientation factor (f).

$$f = \frac{D_{\parallel} - D_{\perp}}{D_{\parallel} + 2D_{\perp}} = 1 - 3/2 \overline{\sin^2 \theta}$$

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{D_o \cos^2 \theta}{\tfrac{1}{2} D_o \sin^2 \theta} = \frac{2 \cos^2 \theta}{\sin^2 \theta} = 2 \cot^2 \theta$$

$$\cot^2 \theta = \tfrac{1}{2} \left(\frac{D_{\parallel}}{D_{\perp}} \right)$$

$$\cot^2 \theta = \frac{D.R.}{2}$$

$$\cot \theta = \sqrt{\frac{D.R.}{2}}$$

$$\theta = \cot^{-1} \sqrt{\frac{D.R.}{2}}$$

θ = average orientation angle

From the dichroic ratios the value of θ for the various films was calculated and plotted versus draw ratio and density.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

A comparison of the films obtained by solution casting, use of the Buehler press, and the hot pressing with the ferrotype plates showed that the solution casting led to films with irregular surface effects. Those with the Buehler press were poorly fused and of too small cross-section for drawing. The hot pressed films on the other hand gave films of uniform thickness, uniform surface, well fused, and of desirable cross section. This method of film preparation was chosen as best in this study.

Table VI lists the solutions and the order of addition of the mixtures used in preparing the gradient tube. In Table VII the densities of the bulbs used in the calibration are given. Figure 6 is the calibration curve for the density gradient tube. The plot shows that a linear gradient of density was obtained. The densities for the various samples are given in Table VIII. The densities compared, showed an increase by increasing the degree of extension. In Figure 7 densities are plotted versus draw ratio for the samples drawn at 80°-95°. The density increases with draw ratio from 0.9044 g/cc up to a maximum of 0.9075. This maximum is achieved at a draw ratio of about 2.0. After a draw ratio of 2.0, no appreciable change in density occurs. Figure 8 is a similar plot for the samples drawn between 130° and 140°C. Here the density increases rapidly from 0.8975 g/cc to 0.9065 g/cc.
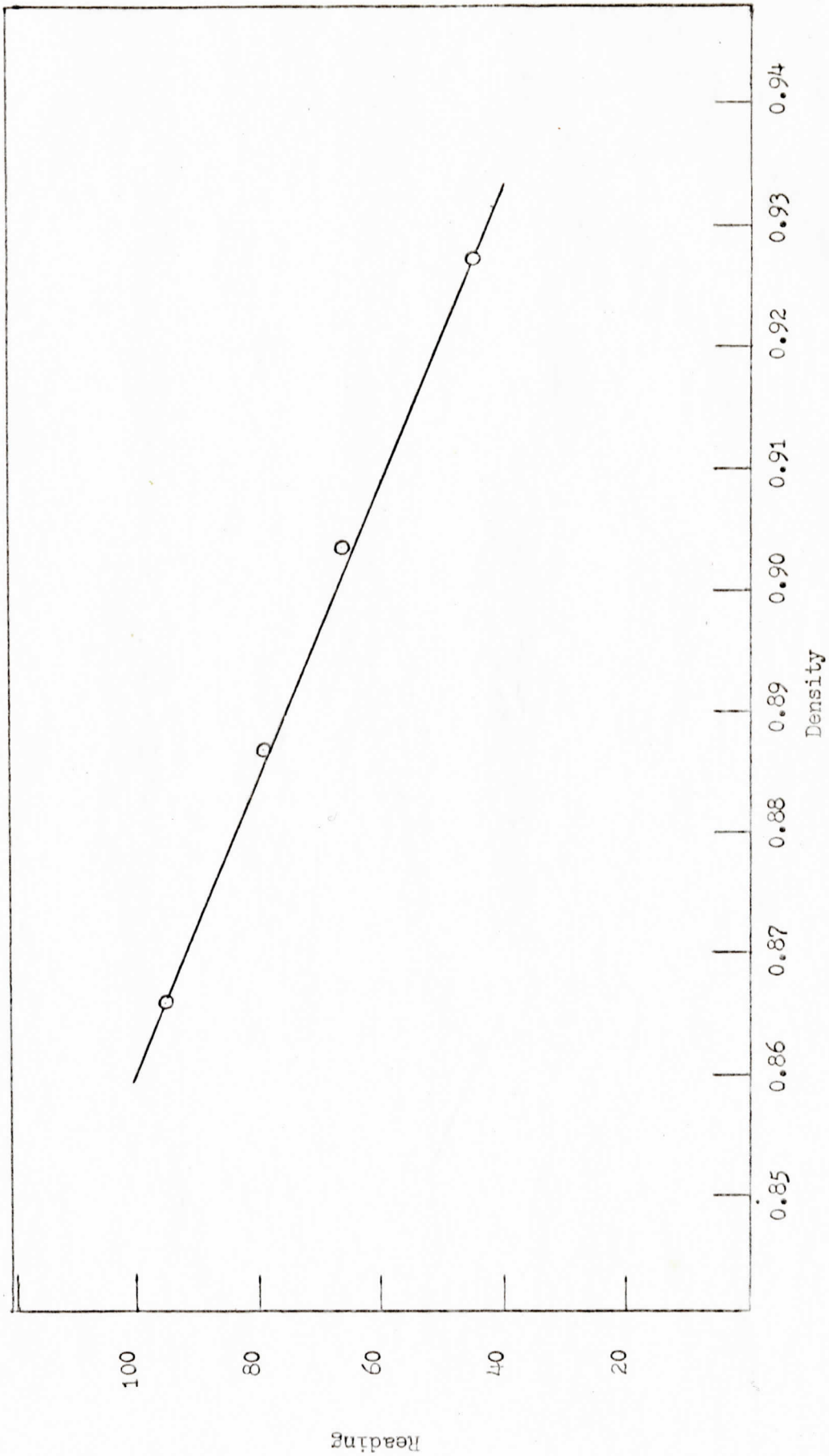
FIGURE 6

A CALIBRATION CURVE FOR THE

DENSITY GRADIENT TUBE

TABLE VIII

THE DENSITIES AND DRAW RATIOS FOR VARIOUS SAMPLES OF
POLYPROPYLENE DRAWN AT TEMPERATURES OF
80°-95°C. and 130°-140°C.

Samples drawn at 80°-95°C.	Draw Ratio	Density
F-17	0.15	0.9044
F-23	0.75	0.9047
F-27	1.00	0.9050
F-32	1.75	0.9070
F-41	2.25	0.9077
F-36	3.25	0.9075
F-34	4.00	0.9075

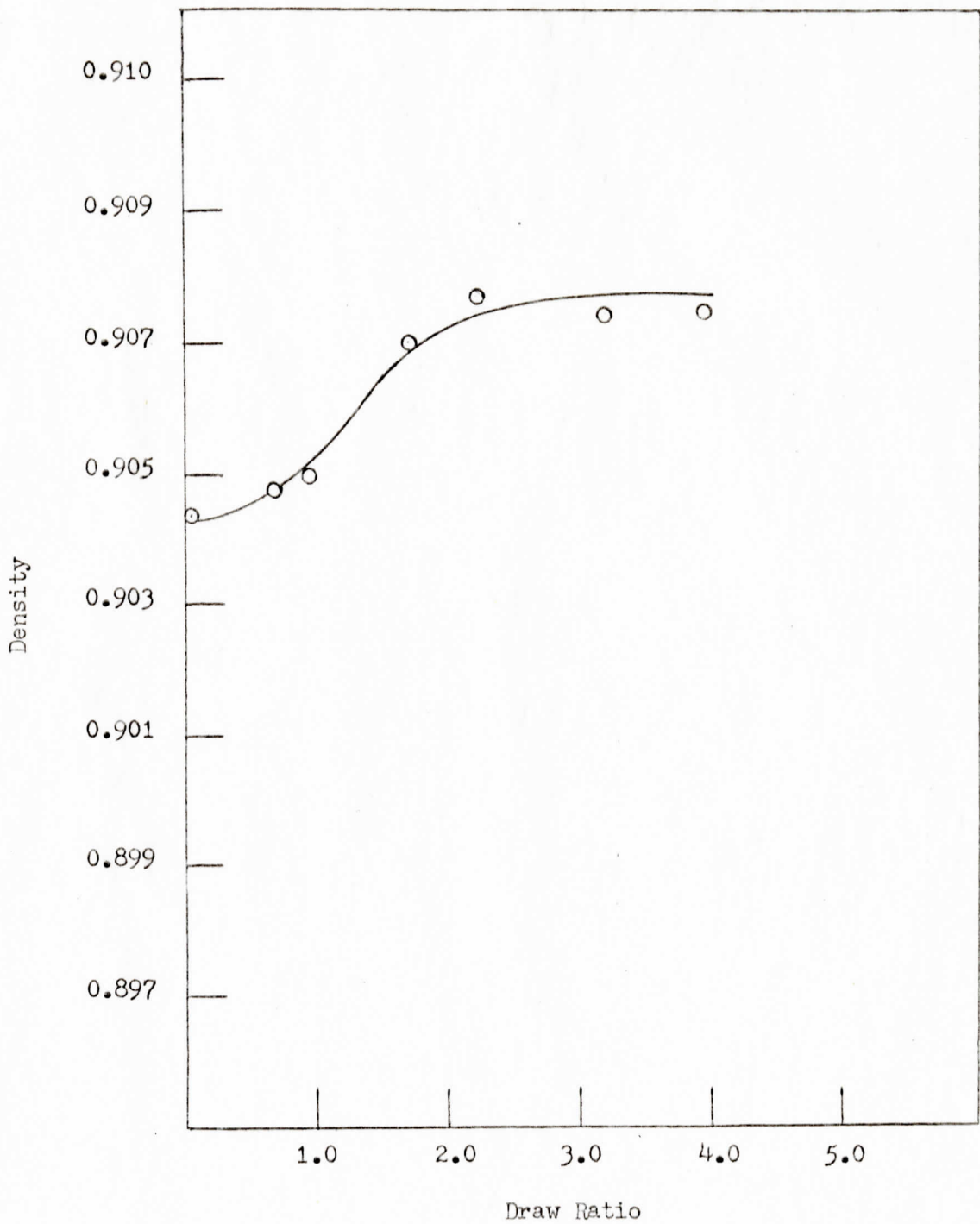| Samples drawn at 130°-140°C.	Draw Ratio	Density
F-6	1	0.9015
F-8	2	0.9050
F-10	3	0.9058
F-12	4	0.9065
F-14	5	0.9064

FIGURE 7

THE RELATIONSHIP BETWEEN DENSITY AND DRAW RATIO
FOR POLYPROPYLENE SAMPLES DRAWN AT A
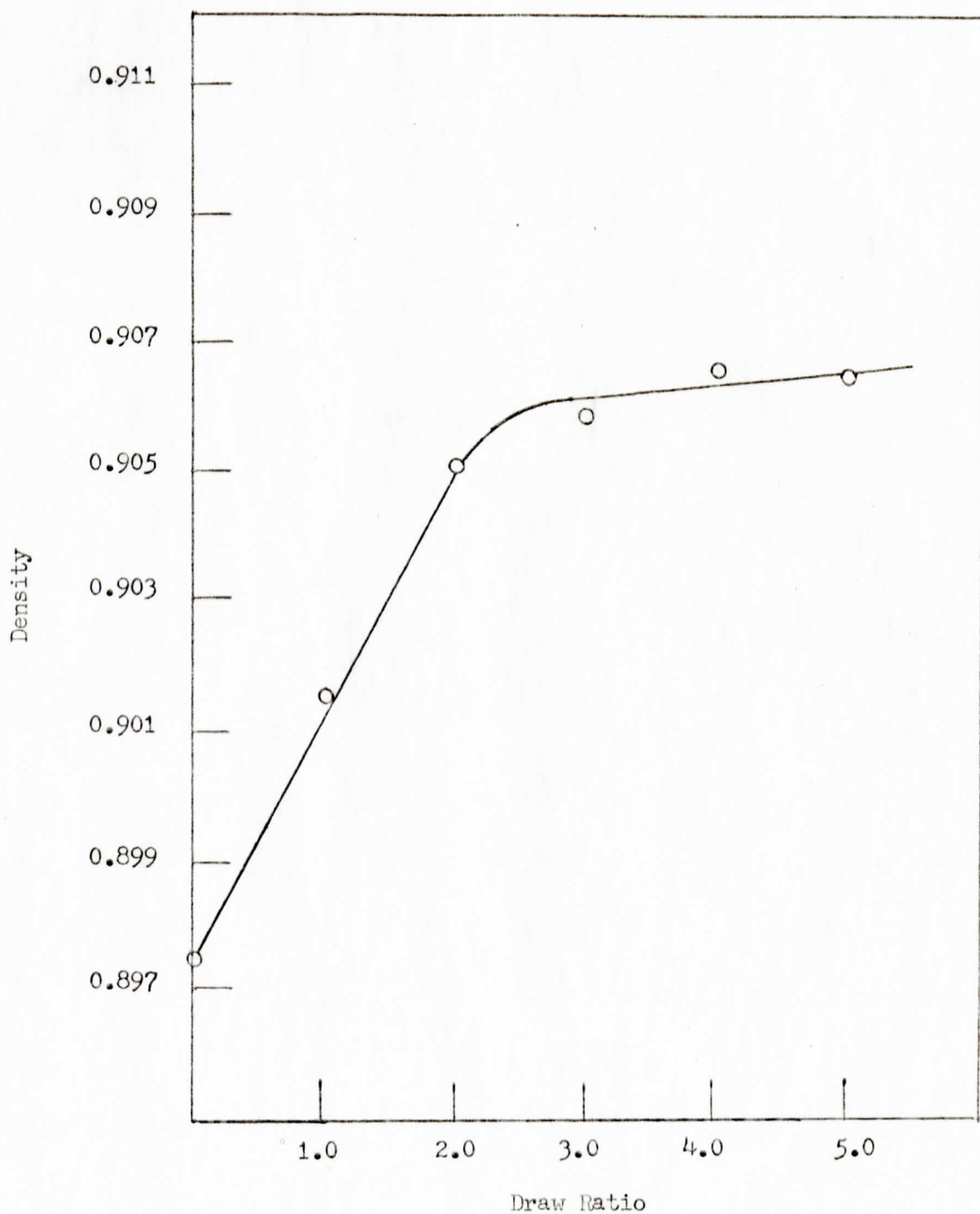TEMPERATURE OF 80°-95°C.

FIGURE 8

THE RELATIONSHIP BETWEEN DENSITY AND DRAW RATIO
FOR POLYPROPYLENE SAMPLES DRAWN AT A
TEMPERATURE OF 130°-140°C.

Once again, however, the maximum appears to be approached at a draw ratio between 2 and 3.

Table IX gives the draw ratio, dichroic ratio, and average orientation angle for the 840 cm^{-1}, 1255 cm^{-1}, and the 1303 cm^{-1} absorption bands for films drawn between 80° and 95°C. Similar data for samples drawn between 130° and 140°C. are given in Table X. In Figure 9, 10, and 11 the average angle of orientation is plotted versus draw ratio for the 840 cm^{-1}, 1255 cm^{-1}, and the 1303 cm^{-1} bands for the 80°C. samples. Similar plots for the 130°C. samples are shown by Figures 12, 13, and 14. All of these plots show that the orientation angle θ decreases with increasing draw ratio. Although there is some scatter of the experimental points, the orientation angle decreases with increasing draw ratio and approaches a very nearly constant value at very low draw ratios between 1 and 2 for the 80°C. samples. The decrease of angle is more gradual for the 130°C. samples. This is probably due to the dis-orienting effect followed by an orienting effect in the 130°C. samples because of the higher drawing temperature.

It is interesting to note also that the maximum orientation attained depends upon the drawing temperature; being greater for the higher temperature.
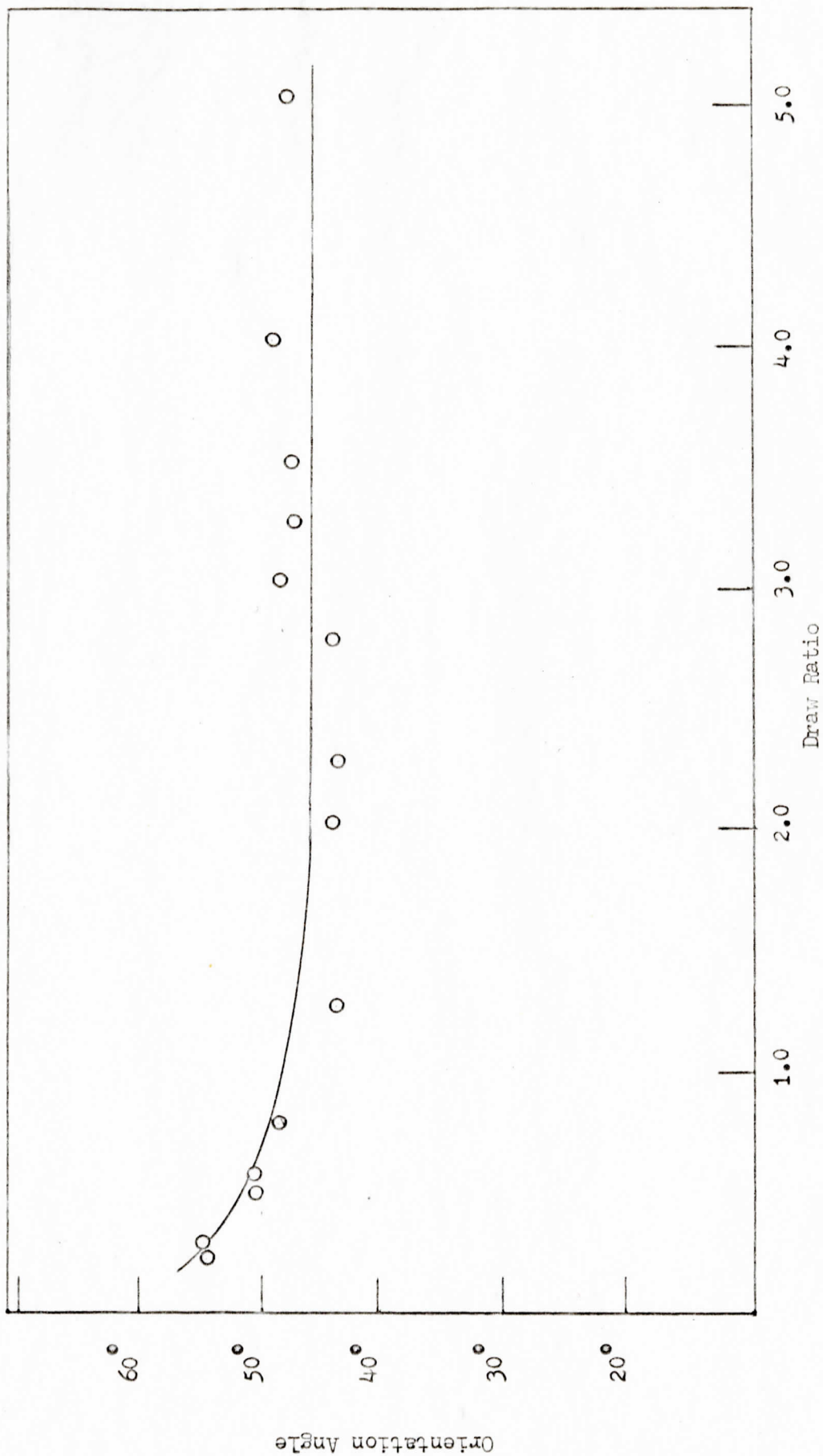
THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE
AT A FREQUENCY OF 840 cm^{-1} FOR POLYPROPYLENE SAMPLES
DRAWN AT A TEMPERATURE OF 80°–95°C.

FIGURE 9

Orientation Angle

Draw Ratio
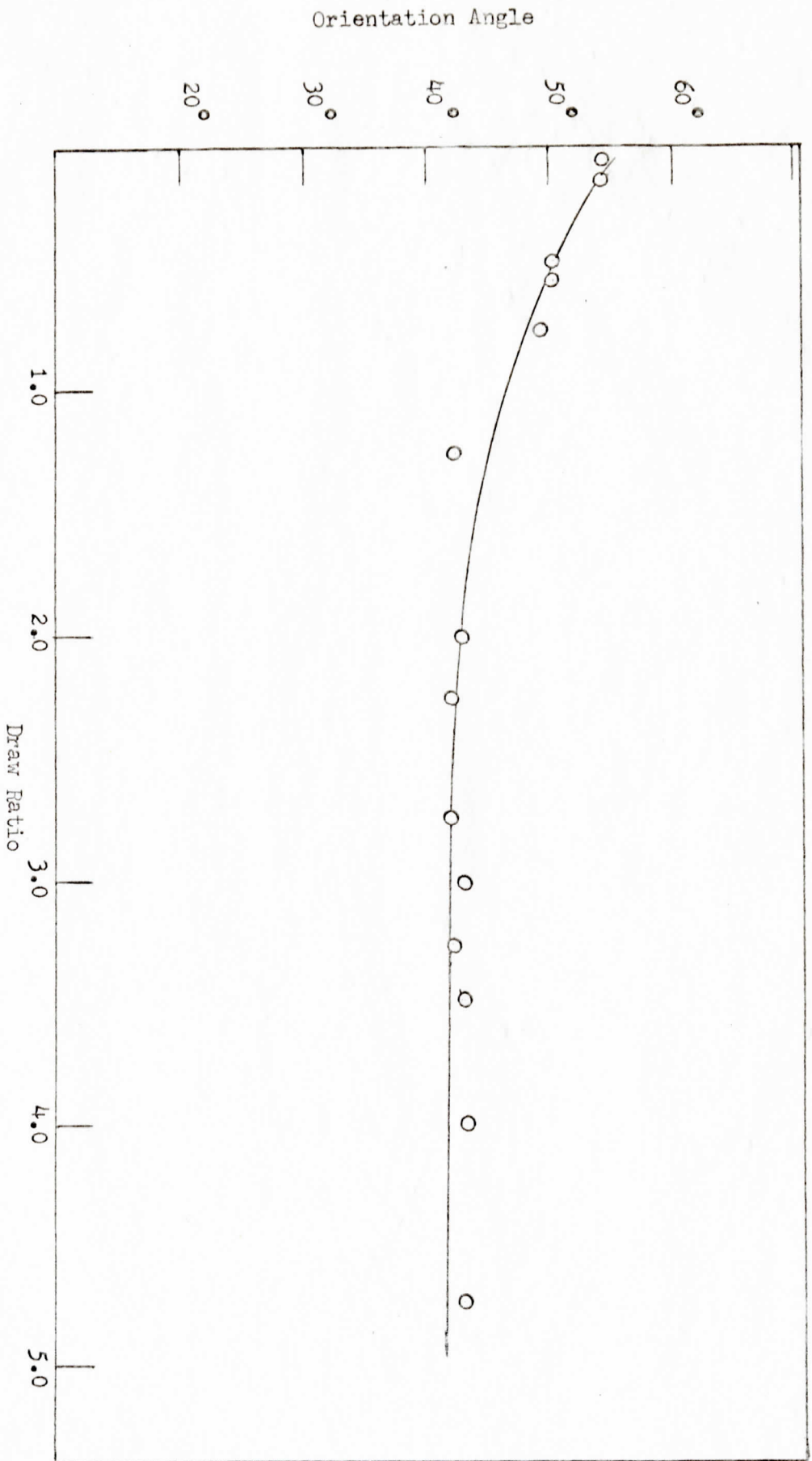
FIGURE 10

THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE

THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE
AT A FREQUENCY OF 1303 cm^{-1} FOR POLYPROPYLENE SAMPLES
DRAWN AT A TEMPERATURE OF 80°-95°C.

FIGURE 11

THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE
AT A FREQUENCY OF 840 cm^{-1} FOR POLYPROPYLENE SAMPLES
DRAWN AT A TEMPERATURE OF 130°-140°C.

FIGURE 12

Draw Ratio

FIGURE 13

THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE
AT A FREQUENCY OF 1255 cm^{-1} FOR POLYPROPYLENE SAMPLES
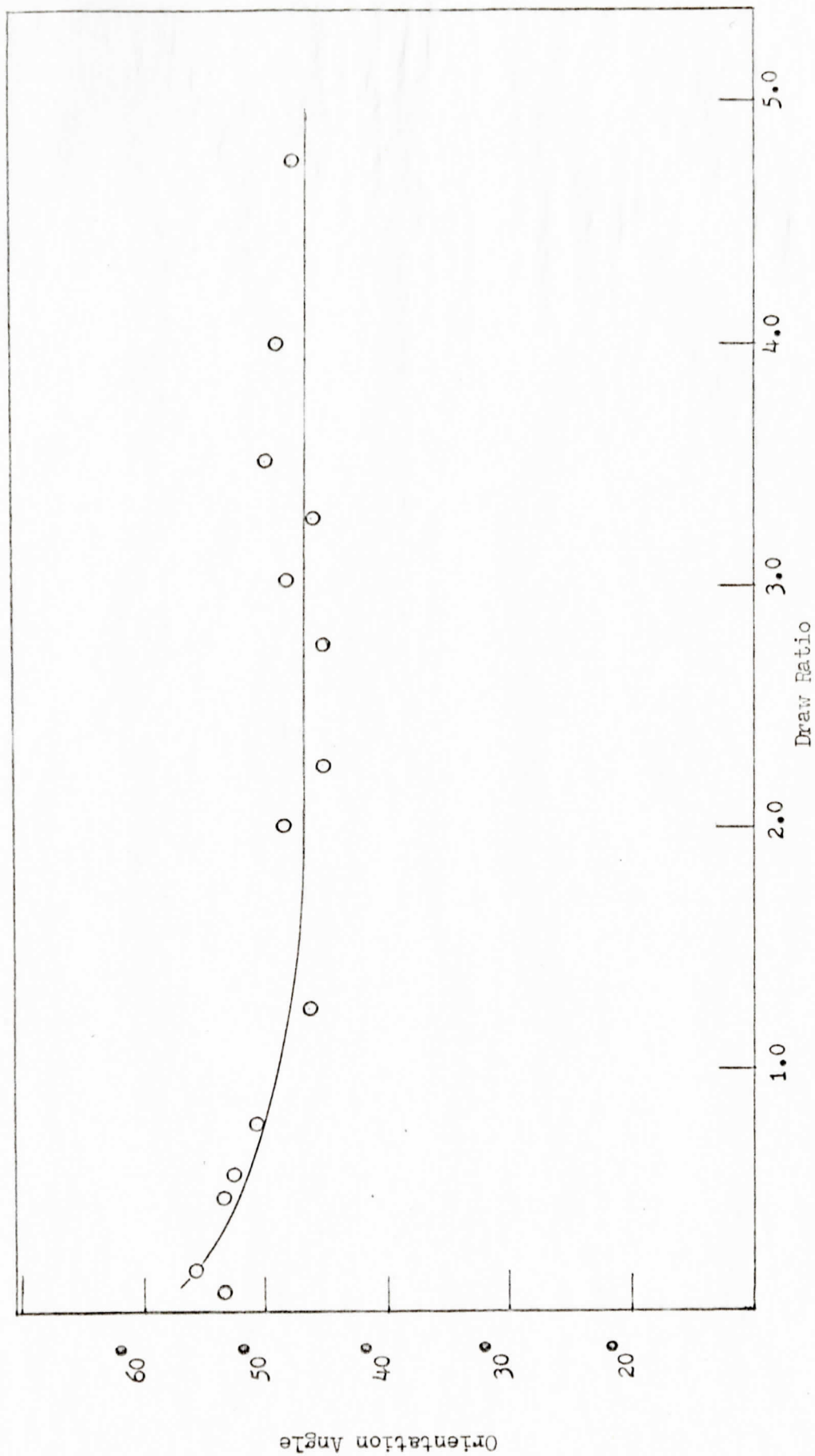DRAWN AT A TEMPERATURE OF 130°-140° C.

Orientation Angle

Draw Ratio
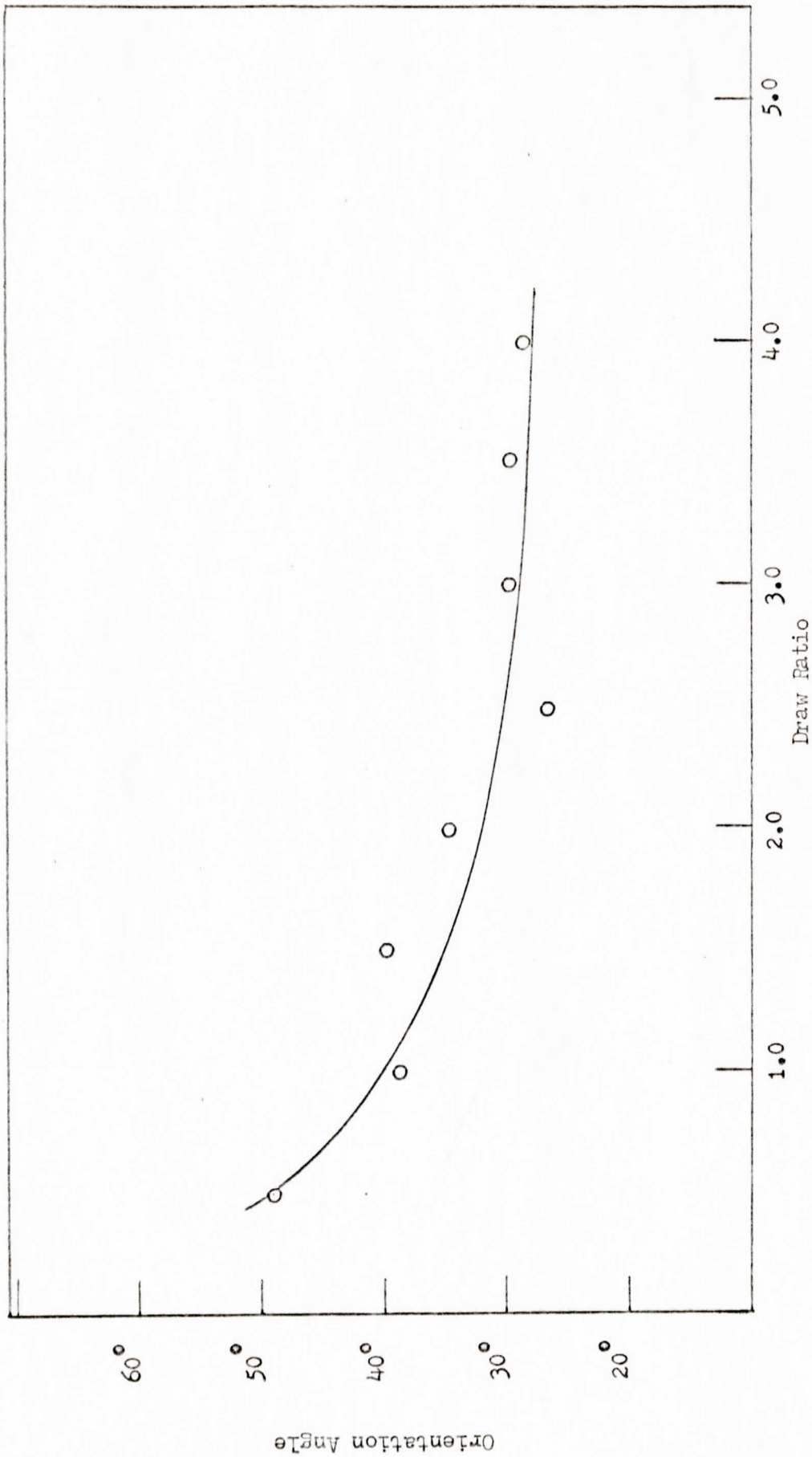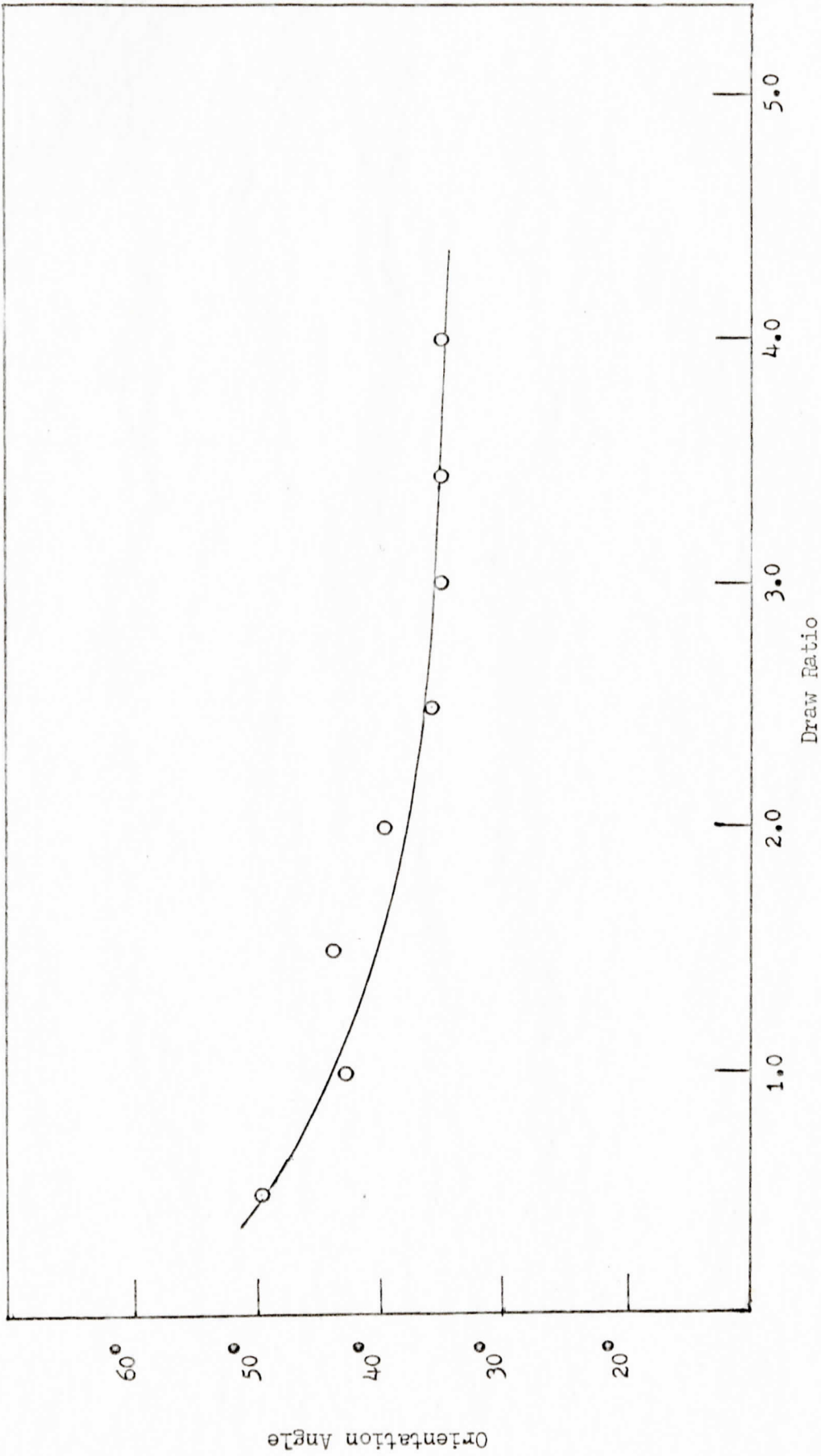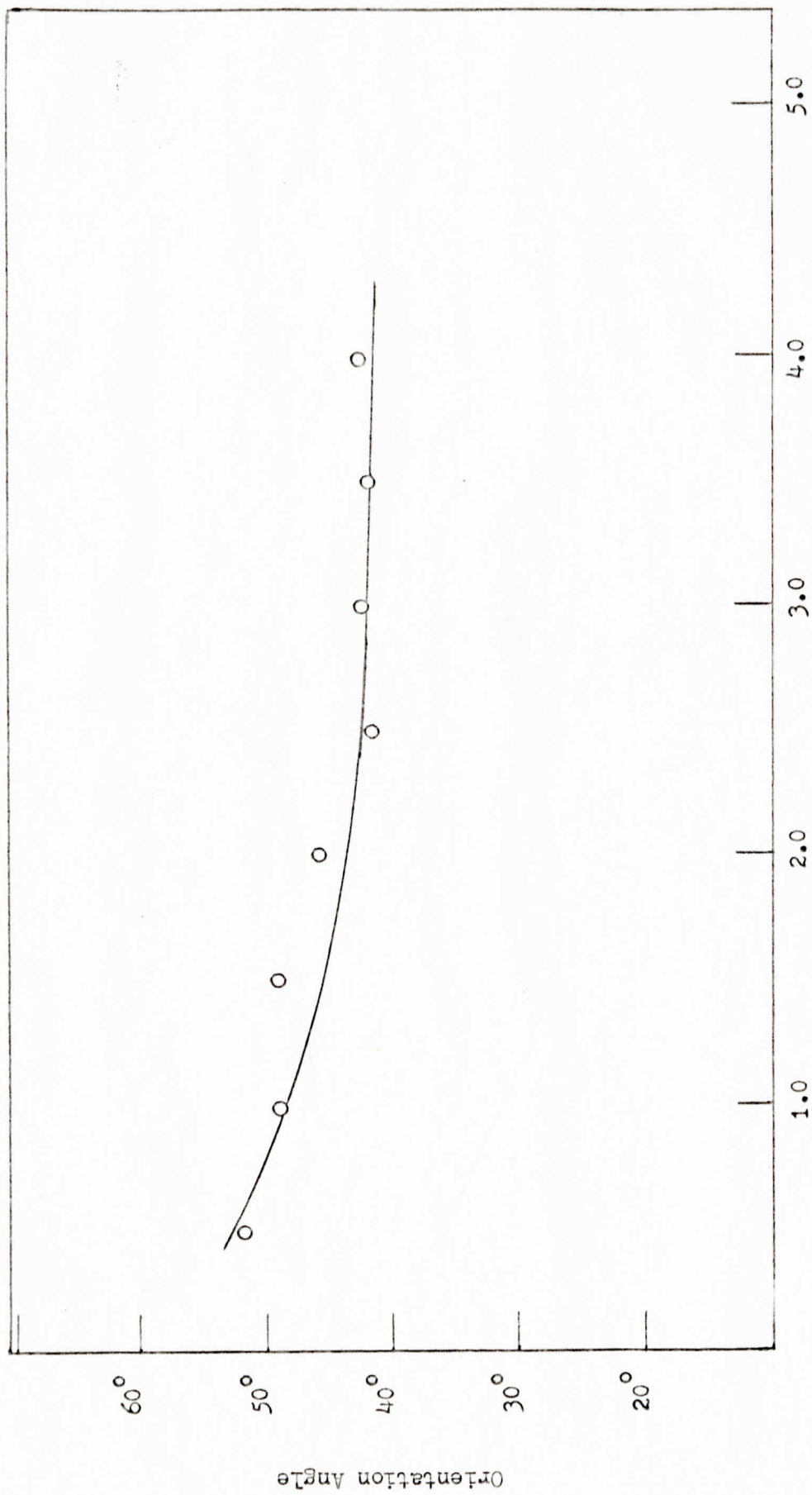
FIGURE 14

THE RELATIONSHIP BETWEEN THE DRAW RATIO AND THE ORIENTATION ANGLE
AT A FREQUENCY OF 1303 cm^{-1} FOR POLYPROPYLENE SAMPLES
DRAWN AT A TEMPERATURE OF 130°-140°C.

Orientation Angle

TABLE IX

DICHROIC RATIO AND ORIENTATION ANGLE FOR POLYPROPYLENE FILMS DRAWN AT A TEMPERATURE OF 80°-95°C.

Sample	Draw Ratio	840 cm⁻¹		1255 cm⁻¹		1303 cm⁻¹	
		D.R.	θ	θ	D.R.	θ	D.R.
F-17	0.15	1.07	55°	55°	1.05	54°	1.00
F-44	0.30	1.12	56°	55°	1.05	56°	1.08
F-19	0.45	0.88	53°	52°	0.87	54°	0.98
F-22	0.60	0.88	53°	52°	0.85	53°	0.88
F-23	0.75	0.68	49°	50°	0.76	51°	0.78
F-28	1.25	0.53	45°	46°	0.56	47°	0.59
F-33	2.00	0.53	45°	47°	0.57	48°	0.64
F-41	2.25	0.49	44°	45°	0.53	46°	0.55
F-39	2.75	0.51	44°	45°	0.50	46°	0.52
F-38	3.00	0.69	49°	47°	0.57	49°	0.63
F-36	3.25	0.60	47°	45°	0.50	47°	0.57
F-37	3.50	0.59	47°	47°	0.59	51°	0.74
F-34	4.00	0.72	50°	48°	0.61	50°	0.72
F-35	4.75	0.62	48°	46°	0.56	48°	0.61

TABLE X

DICHROIC RATIO AND ORIENTATION ANGLE FOR
SAMPLES DRAWN AT A TEMPERATURE
OF 130°-140°C.

Sample	Draw Ratio	840 cm^{-1}		1255 cm^{-1}		1303 cm^{-1}	
		D.R.	θ	D.R.	θ	D.R.	θ
F-5	0.5	0.67	49°	0.14	50°	0.78	52°
F-6	1.0	0.34	39°	0.43	43°	0.66	49°
F-7	1.5	0.35	40°	0.47	44°	0.67	46°
F-8	2.0	0.25	35°	0.37	40°	0.41	42°
F-9	2.5	0.14	27°	0.27	36°	0.41	42°
F-10	3.0	0.16	30°	0.25	35°	0.42	43°
F-11	3.5	0.17	30°	0.25	35°	0.40	42°
F-12	4.0	0.16	30°	0.24	35°	0.43	43°

CHAPTER V

SUMMARY AND CONCLUSIONS

The average total molecular orientation of films of stereoregular polypropylene has been investigated as a function of density and degree of extension.

In this study films of polypropylene appropriate for infrared analysis and density measurements were prepared by a hot pressing method with ferrotype chromium plates. The films were drawn variously by a special stretching frame described. Dichroic ratios were obtained by analysis of polarized infrared spectra obtained with a high resolution Beckmann infrared spectrometer, IR-7 used in association with polarizer, beam condenser and a microsample assembly described in this study. Densities were measured by a carbon tetrachloride toluene linear density gradient tube prepared for this study.

Average orientation angles were calculated from the infrared dichroic ratios and these were plotted versus draw ratios and also densities.

The results obtained show that the orientation angle decreases with increasing draw ratios and increasing density. These results indicate that the extending process produces an orientation of both the crystalline and amorphous regions, and increases the degree of crystallinity.

II. CONCLUSIONS

A correlation was found between the orientation angle and the draw ratio. It was also found that samples drawn under low heating conditions showed lower maximum orientation as judged by the dichroic ratios than did samples which were under more severe heating conditions. The temperature at the time of drawing plays an important role in the amount of orientation a given sample will achieve.

It was concluded that a draw ratio between 2 and 3 results in a near maximum of orientation in Escon-125 polypropylene. A draw ratio of 2.5 gave a lower value for the average angle of orientation in samples drawn under more intense heat.

The density was found to depend, among other things, on the orientation. It was noted that the density approaches a maximum value at the same draw ratio which gives a minimum orientation angle.

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