AN INVESTIGATION OF THE STRUCTURE OF FRACTIONATED STEREOREGULAR POLYPROPYLENE BY POLARIZED INFRARED RADIATION

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

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

by
Wallace McBride Putnam
August, 1967

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ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. J. E. Johnson for his advice, encouragement, and assistance throughout the course of this research.

The author also wishes to express his appreciation to Dr. H. L. Bowkley, Dr. G. B. Miles, and Dr. D. L. Wright for their advice and assistance.

To my parents, wife, and son.

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ABSTRACT

Structure characterizations and comparisons of a low and a high molecular weight fraction of stereoregular polypropylene are presented.

Low and high molecular weight fractions obtained by extraction of polypropylene polymers, Escon-105, Escon-113, and Escon-125 with n-heptane at elevated temperature were cast into films and subsequently stretched various amounts.

Infrared spectra were obtained for the undrawn and drawn films using non-polarized and polarized infrared radiation. In addition, infrared spectra for the fractions were obtained as a function of temperature. Densities and dichroic ratios were determined and from these percent crystallinities and average orientation angles were calculated. In addition, infrared spectra were indexed with respect to frequency and relative intensity and compared for the fractions.

The results of this study show that crystallinities range from 43.6 to 52.0% and orientation angles range from 18 to 54 degrees. Also, the tacky low fraction was brittle and could not be oriented. Further, a comparison of the spectra of the two fractions showed intensity reversals of certain infrared absorptions, disappearances of others, and appearances of new absorptions. The melting point of the low and high fractions were 120° and 170° C., respectively. Correlations of orientation angle and draw ratio with crystallinity were made.

The results of this study suggest that the low fraction may possess a different crystalline modification. Also, the study suggests as others have found that a correlation between orientation and draw ratio exists. Finally, no correlation was shown between orientation and crystallinity—in disagreement with other studies. A possible explanation is presented.

CHAPTER I

INTRODUCTION

The purpose of this study was to investigate the molecular structure of low and high molecular weight fractions of stereoregular polypropylene. The methods of investigation consist of the following:

(1) The obtaining of low and high molecular weight fractions by extraction with heptane,

(2) The characterization of the fractions with respect to density, weight average molecular weight, infrared absorption spectra, and infrared absorption spectra as a function of temperature,

(3) The obtaining and drawing of films to various draw ratios,

(4) The obtaining of the crystallinity of films from density,

(5) The obtaining of dichroic ratios from polarized infrared absorption spectra, and

(6) An attempt to correlate crystallinity, draw ratio, and average orientation angle.

CHAPTER II

LITERATURE REVIEW

I. PREPARATION OF STEREOREGULAR POLYPROPYLENE

Stereoregular polypropylene is a vinyl-type, high polymer prepared by the polymerization of propylene with a Ziegler-type stereoregular catalyst, obtained by the interaction of aluminum alkyls and salts of Group IV and VI metals in an inert solvent (20)(21).

Although there is still some confusion as to the mechanism of this type of polymerization reaction, Natta and coworkers (15) propose that the high regularity of the structure of isotactic polypropylene, a stereoregular polymer, is allowed by a peculiar anionic co-ordination mechanism of the stereospecific polymerization reaction of α-olefins. In addition, it is proposed that the reaction goes through successive additions of monomeric units to metal-carbon bonds of complexes formed on the surface of a crystal having a layer lattice, such as α-$TiCl_3$, by the action of a metal alkyl, such as $Al(C_3H_7)_3$.

Polymerization reactions involving amorphous catalysts and an anionic co-ordination mechanism yield non-stereospecific polymers, which usually have head-to-tail arrangements of the monomeric units. In this type polymer, the propylene monomeric units may assume two equivalent specular conformations that cannot be superimposed upon each other. The resulting polymer is formed by an unordered succession of the monomeric units of the two types and the chain, therefore, has a random steric structure. However, with the use of heterogeneous stereospecific catalysis, as mentioned above, propylene is first assumed to co-ordinate by means of a π-bond with the transition metal of the catalytic complex followed by the addition of a polarized olefin molecule to the growing polymer chain (15). The polarized olefin molecule can, therefore, assume only one of the two conformations, as previously mentioned. Therefore, the successive monomeric units along the polymer chain assume the same steric configuration.

II. THE PHYSICAL STRUCTURE OF POLYPROPYLENE

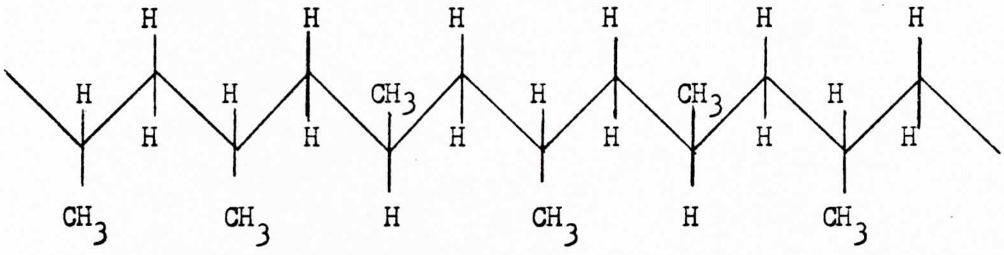
Stereoregular polypropylene has the conventional two phase order-disorder physical structure. The ordered (crystalline) regions have the chain molecules aligned into a three-dimensional lattice arrangement, while the disordered (amorphous) regions are areas of little or no alignment (29). This order-disorder structure is a result of the nature of the particular type of chain molecule and the type of intermolecular forces of attraction between chain molecules. It is, therefore, of importance to understand the nature of the chain configuration and conformation.

The configuration of polymers may be atactic, syndiotactic, or isotactic (21). These terms characterize the configuration of the polymer with respect to the positions of the groups attached to the backbone carbon chain. These configurations for polypropylene are illustrated in Figure 1. Most commercial polypropylenes are of the isotactic-atactic species; however, a syndiotactic species is reported to have been synthesized and isolated (14). The relative amounts of the three configurations in a given polymer are fixed by the polymerization conditions and may be altered only by changing these conditions (24).

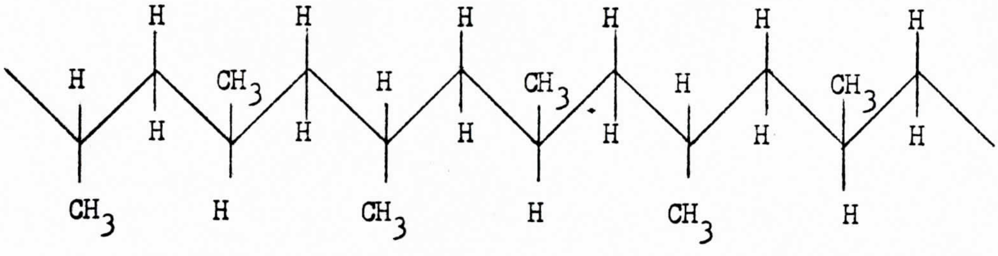
FIGURE 1

THE CONFIGURATIONS OF POLYPROPYLENE

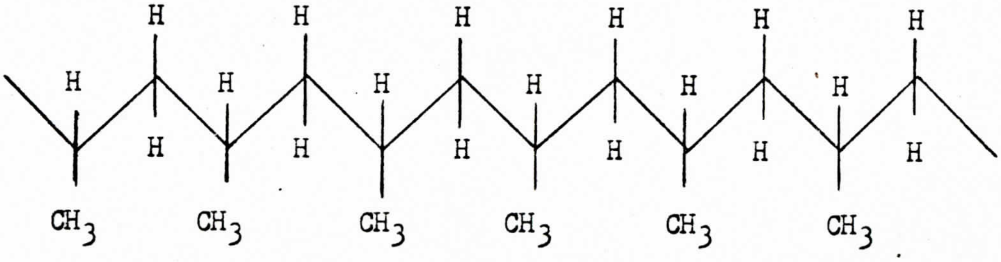
A. Atactic



B. Syndiotactic



C. Isotactic



Chain conformations of polymers may be planar, helical, twisted, or distorted. The chain conformation of stereoregular polypropylene is helical (2)(9)(11)(13)(16)(22).

III. METHODS FOR INTERPRETATION OF PHYSICAL PROPERTIES PERTINENT TO THIS STUDY

Density changes upon drawing polymer. Physical properties of polymers may be interpreted by investigation of the changes in the order-disorder structure. Drawing of polymer films or fibers aligns ordered regions parallel to the direction of drawing while disordered regions are partially aligned so as to augment the ordered regions and decrease the disordered regions. Therefore, drawing produces increased crystallinity and an orientation of both the crystalline and amorphous regions. Certain thermal and mechanical treatments may bring about alterations in the nature of the crystalline regions, such as a different crystalline structure. Sobue and Tabata (27) reported that the ordinary and quasi-crystalline structures coexist in low density-low draw ratio polypropylene films. The quasi-crystalline structure was also found to irreversibly transform to the ordinary crystalline structure upon being annealed at 150° C. for 15 minutes.

A relationship between density and draw ratio has been reported for crystalline polypropylene. Sobue and Tabata (26) found the density increased linearly with draw ratio reaching a maximum density at draw ratios of 4 to 5. However, Schmidt (24) considers that the maximum orientation is obtained only at maximum draw ratio.

Solution properties. Natta and coworkers (19) were the first to report a marked difference of solubilities for isotactic and atactic linear polypropylenes. They reported that for a given polymeric mixture, the crystalline polymers are always less soluble than the amorphous polymers, independently of molecular weight. Extractions of polypropylenes are based on this solubility difference. Crystalline polypropylene is insoluble in acetone, ethyl acetate, and ethyl ether; slightly soluble in boiling n-heptane; and soluble in toluene. Amorphous polypropylene is slightly soluble in acetone and ethyl acetate; soluble in ethyl ether and boiling n-heptane; and very soluble in toluene.

Weight average molecular weights have been determined from intrinsic viscosities for the solid amorphous and crystalline polypropylenes. These values are as low as 2,000 for the "amorphous" material, and in the range of 100,000 for the crystalline (20).

Infrared absorption studies. Several infrared absorption studies have been made of stereoregular polypropylene (1)(2)(3)(4)(5)(7)(8)(9)(10)(11)(23)(24)(25) because of the striking crystallinity effects (29). These studies have utilized both non-polarized and polarized infrared radiation.

The non-polarized infrared absorption studies, pertinent to this study, have been performed with respect to band assignments and relative intensities of absorption bands of crystalline, "amorphous," and molten polypropylene. Table I shows the more prominent absorption bands for crystalline and molten polypropylene films as reported by Abe and Yanagisawa (1). It has generally been assumed that the infrared spectra of amorphous and molten polypropylene are identical. The absorption bands in a spectrum of "completely" isotactic material at 810, 842, 895, 938, 995, 1045, 1103, 1220, 1258, 1295, 1305, 1330, and 1366 cm.$^{-1}$ either become extremely weak or are eliminated in the spectrum of "completely" atactic

TABLE I

THE INFRARED SPECTRA OF POLYPROPYLENE FILMS

Normal State		Melted State	
Frequency, cm^{-1}	R.I.	Frequency, cm^{-1}	R.I.
809	s	810	mb
843	vs	900	b
900	s	974	vs
943	mw	1002	vwsh
976	vs	1153	vs
1000	vs	1258	m
1048	ms	1333	sh
1105	ms	1366	sh
1158	msh	1377	vvs
1170	vs	1458	vvs
1222	mw		
1262	sm		
1306	wsh		
1312	sm		
1333	wsh		
1366	msh		
1379	vvs		
1462	vvs		
2640	wm		
2730	s		
2845	—		
2980	—		
3152	m		
3200	m		

polypropylene (11). Two absorption bands have been found to be relatively temperature-insensitive and have, therefore, been used as internal thickness standards. These bands are at 974 cm.$^{-1}$ (23) and 1171 cm.$^{-1}$ (4).

Polarized infrared absorption studies of drawn samples give information of the orientation of group transition moments. Orientation studies have been performed with respect to band assignments, relative intensity, polarization effect, and interpretation of orientation active groups. One such study is summarized in Table II (9).

Infrared orientation studies are performed by polarizing the infrared radiation, usually by means of a AgCl plate polarizing element, and placing the oriented sample in the polarized beam so as to align the draw direction of the sample, first parallel and then perpendicular, with the electric vector of the polarized beam. The dichroic ratio, the magnitude of which indicates the orientation of an attached group relative to the chain axis, is given by the equation (29)

$$R=\frac{A_{\parallel}}{A_{\perp}}$$

where R is the dichroic ratio, $A_{\parallel}$ and $A_{\perp}$ are the absorbances of an absorption band when the draw direction of the sample is aligned parallel and perpendicular, respectively, with the electric vector of the polarized beam.

The average orientation angle, the angle between the group transition moment direction and the chain axis, can be calculated from dichroic ratios when the above definition of dichroic ratio is used by the equation

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

where θ is the average orientation angle, and R is the dichroic ratio. This equation was derived (6) assuming that an uniaxially oriented structure is produced by drawing polypropylene films in one direction.

TABLE II

THE POLARIZED INFRARED SPECTRUM OF CRYSTALLINE POLYPROPYLENE (FUNDAMENTALS)

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

CHAPTER III

EXPERIMENTAL

I. MATERIALS AND EQUIPMENT

In this study Escon 105, 113, and 125 stereoregular polypropylene polymers in pelletized form obtained from Enjay Chemical Company were used. In addition, Fisher technical grade xylene and Fisher Certified heptane and toluene as polymer solvents, and Fisher Certified ethanol (95%) for density gradient mixtures were employed.

The equipment used was an all glass reflux apparatus with heating mantle for the extraction process; 3" x 3" glass plates, 3" x 4" Apollo Ferrotype plates, and a Buehler metallurgical press with heating attachment for film preparations; drawing frame and infrared heating lamp for drawing of films; density gradient tube with density bulbs, a Fisher thermoregulated water bath, and pycnometer for density gradient preparation and calibration; a Beckman, Model IR-7, infrared spectrophotometer with NaCl optics, used in association with a beam condenser, silver chloride polarizer, microsample holder, Perkin-Elmer heating cell, and 25 mm x 5 mm NaCl discs for infrared absorption studies; and a Cannon 100-J, 685 pipet viscometer used in association with a thermoregulated glycerine bath for molecular weight estimations. All weighings were performed on a Mettler Gram-atic balance.

II. METHOD

Extraction of whole polymers. 30 grams of the whole polymer (Escon

105, 113, or 125) and 300 ml of heptane were refluxed for twenty hours in a glass reflux apparatus heated by a heating mantle. Twenty hours was found to be sufficient time for efficient extraction. The hot heptane soluble fraction was withdrawn, stored for distillation of the heptane, and the heptane insoluble fraction was air dried and stored for further use. The heptane was distilled from the heptane soluble fraction so as to prevent charring of the residue. The residue was then heated on a steam bath to effect further removal of heptane.

Preparation of films. Films of all three polymers-- whole, heptane insoluble, and heptane soluble polymers--were prepared by hot pressing, compression molding, and solution casting. The hot pressing method consisted of heating 0.5 to 1.0 gram of polymer on a 3" x 4" Apollo Ferrotype plate on a hot plate. The molten polymer was then covered by a second similar plate. Pressure was then applied to the top plate so as to give a uniform film of thickness appropriate for the infrared absorption studies. The molten film was quenched in distilled water at 20° C. while still applying pressure by means of tongs.

The compression molding method consisted of heating the cylinder and piston of a Buehler metallurgical press by means of a heating attachment to approximately 180° C. and introducing 0.1 to 0.3 gram of the polymer into the cylinder. Heating was continued until the sample was molten. Pressures used ranged from 5,000 to 9,000 lb./in.^{2} Cooling was immediately effected by means of an aluminum block for varying lengths of time.

A solution casting method was also employed. 0.5% solutions of polymer in xylene or toluene were evaporated on heated glass plates. Varying conditions of temperature and concentration were used.

Films of the heptane soluble fraction were prepared by a combination of hot pressing and solution casting methods. These films were prepared by slowly heating 3" x 3" glass plates on a hot plate and sandwiching 0.3 to 0.5 gram of polymer in xylene or toluene paste form between them while applying pressure. When melting occurred, the plates were quenched in ice water while still applying pressure.

Drawing of films. Films of the heptane soluble and insoluble fractions of appropriate thicknesses were drawn in a drawing frame while being heated with an infrared heating lamp. Heat was applied until a thermometer under the film, but touching the film, indicated temperatures of 95-100° C. Drawing was accomplished at a drawing rate of approximately 50 cm per minute. Films of varying thickness were drawn to predetermined lengths in order to achieve certain draw ratios. Draw ratio used in this study was taken as length after drawing minus length before drawing divided by length before drawing. Lengths were determined by measuring the distance between two marks placed on the film before heating. Films were air cooled and sufficient time was allowed for relaxation of the films before the length after drawing was measured and recorded.

Determination of densities. Densities were determined by a density gradient method at 30.4 ± 0.1° C. This involved the construction and calibration of the density gradient tube and the measurement of film densities.

The density gradient tube was constructed by slowly siphoning a solution of ethanol and water of continuously changing density into a thermostated tube. The continuous density change was accomplished by connecting two beakers, one containing an ethanol-water solution--approximate density 0.92 g/cm^3 and the other containing ethanol (95%)--approximate density 0.81 g/cm^3, so as to have the 0.81 g/cm^3 density solution siphon into the o.92 g/cm^3 density solution at the same rate as siphoning of the 0.92 g/cm^3 solution into the gradient tube. The denser solution was stirred continuously by a magnetic stirrer.

The density gradient tube was calibrated by glass bulbs of known density. The bulbs were calibrated at 30.4 ± 0.1° C. by a flotation method using ethanol-water solutions. The bulbs were made to acquire a position midway in a depth of solution by adding ethanol and/or water until the density of the solution matched the density of the bulb. The density of the solution was then determined with a pycnometer. The calibrated bulbs were then introduced into the density gradient tube and after equilibration occurred, the scale positions of the bulbs were read and recorded.

Film densities were determined by placing approximately 3 mm^2 samples under the surface of the liquid, and allowing time for the maximum depth to be reached. The position of the film was then read and recorded. The densities were read from the calibration curve of the density gradient tube. Densities were found to be reproducible to ± 0.001 g/cm^3.

Densities were then used to calculate percentage crystallinities. The percentage crystallinity is related to density by the equation,

$$V_x = xV_c + (1-x)V_a,$$

where V_x is the specific volume of the sample of unknown crystallinity, V_c is the specific volume of a completely crystalline sample, V_a is the specific volume of a completely "amorphous" sample, and x is the crystalline fraction of the sample in question. Since specific volume is the reciprocal of density, then

$$\frac{1}{\rho_x} = \frac{x}{\rho_c} + \frac{(1-x)}{\rho_a} .$$

Solving for x yields

$$x = \frac{\rho_c(\rho_x - \rho_a)}{\rho_x(\rho_c - \rho_a)} .$$

Percentage crystallinity is then related to density as

$$\%X = \frac{\rho_c\ (\rho_x-\rho_a)}{\rho_x\ (\rho_c-\rho_a)} \quad x\ 100$$

Percentage crystallinities were calculated from the above equation using the density of the completely "amorphous" sample as the lowest density observed for the heptane soluble films and the density of the completely crystalline samples as 0.936 g/cm^3, which was obtained by Natta (17) from X-ray data. Percentage crystallinities were plotted versus draw ratios for all stretched films.

Infrared absorption studies. The infrared absorption spectra in the range of 600 to 4,000 cm^{-1} were obtained in turn for the undrawn films of the polymer samples by programming the infrared spectrophotometer with the appropriate slit program, gain, period, and scanning speed for double beam operation. Absorption bands were indexed with respect to frequency (cm^{-1}) and relative intensity.

The spectra of the drawn films were obtained by placing the beam condenser and polarizer in the sample beam. The sample was mounted in a microsample holder and placed at the focal point of the condensed beam. Spectra were recorded for the film aligned first with the electric vector of the polarized beam parallel to the direction of drawing and second with the electric vector of the polarized beam perpendicular to the direction of drawing. The absorbances of the various absorption bands were determined for the parallel and the perpendicular scans by a base-line method (29). Absorption bands were indexed with respect to frequency, relative intensity, and polarization effect. From these data dichroic ratios, R, were calculated for various absorption bands after thickness correction. The dichroic ratios were calculated from the equation,

$$R = \frac{A_{\parallel}}{A_{\perp}}\ .$$

The average orientation angle, Θ, was calculated from the equation,

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

Percentage crystallinities were plotted versus average orientation angles.

Dichroic ratios and average orientation angles were calculated at various frequencies (cm^{-1}) for a film of very large draw ratio to ascertain the relative orientation of the groups undergoing a change in transition moment.

Determination of melting range. The melting ranges of the heptane soluble and insoluble fractions were determined by measuring the absorbances of various infrared absorption bands at various temperatures. The instrument was programmed with the appropriate conditions of slit program, gain, period, and scanning speed for double beam operation. A Perkin-Elmer heating cell with NaCl discs and thermocouple were properly placed in the sample beam and the infrared absorption spectra were recorded at temperatures from 35° to 190° C. Temperatures were held constant to ± 2° C.

Prior to the recording of the spectra, the thermocouple was calibrated using glycerine at various constant temperatures. The arbitrary meter readings of the thermocouple scale were plotted versus temperature to obtain a calibration curve.

The NaCl discs were prepared from rough NaCl discs so as to render them appropriate for infrared studies. The rough discs, 25 mm x 6 mm, were ground to approximately 5 mm thicknesses by grinding first with a coarse grade of emery cloth and second with a fine grade of emery cloth. The final polishing step was performed by alternately rubbing the discs with a soft, moistened cloth and quickly rubbing on a soft, dry cloth. A smooth, transparent surface was obtained by using a figure eight grinding and polishing pattern. A film of the polymer was sandwiched between the

NaCl discs using an appropriately sized lead spacer.

The absorbances, as determined by a base line method, were plotted versus temperature to determine the melting ranges of the Escon-113 heptane soluble and insoluble fractions.

Estimation of molecular weights. The weight average molecular weight of each polymer was determined by viscometry. The samples were prepared by dissolving approximately 0.4 gram of the polymer in 50 ml of xylene. Heat was applied to effect solution. The pipet viscometer was of appropriate capillary size to yield efflux times of approximately 25 to 75 seconds for the solutions used. The viscometer was thermostated at 115 ± 2° C. in a glycerine bath. The efflux time for the solvent was determined by introducing 5 ml of the solvent into the viscometer and allowing time for thermal equilibration to occur. The efflux times were measured with a stopwatch. The polymer solutions were treated as previously described to determine their efflux times. The viscometer was thoroughly cleaned, rinsed, and dried after each determination.

The weight average molecular weights were calculated using the relationships (28)

$$\eta_{sp} = \frac{\text{efflux time of solution}}{\text{efflux time of solvent}} - 1$$

and

$$\frac{\eta_{sp}}{c} = K_m \bar{P}_w,$$ where η_{sp} is the specific viscosity, c is the concentration of solute in grams per liter of solvent, K_m is a proportionality constant, and $\bar{P}_w$ is the weight average degree of polymerization. The weight average degree of polymerization is defined as the weight average molecular weight divided by the monomer molecular weight.

In this study the weight average molecular weight of Escon-125 whole polymer was used to calculate the proportionality constant, K_m. The weight average molecular weight was given as 250,000 (12) and the monomer molecular weight was 42. Therefore, substitution of these values into the above equations with the specific viscosity determined experimentally as described above yields 4.07×10^{-5} for the value of K_m for polypropylene in xylene at 115° C.

CHAPTER IV

RESULTS AND DISCUSSION

I. CHARACTERIZATION OF HEPTANE SOLUBLE AND INSOLUBLE FRACTIONS

Extraction of whole polymers. Samples of the whole polymers were extracted with heptane into heptane soluble and insoluble fractions. During the extraction process no visual evidence of swelling was observed for the whole polymers. The heptane soluble fractions ranged from 1 to 5%, by weight, of the whole polymers extracted. The heptane insoluble fractions appeared to be changed very little by extraction, however, the heptane soluble fractions were sticky rather than a fine crystalline material.

Preparations of films. Of the several methods of film preparation employed, the hot pressing method was best for preparing films of the whole and heptane insoluble polymers while the combined methods of hot pressing and solution casting were best for preparing films of the heptane soluble polymers. These methods were used to prepare films of satisfactory properties appropriate for density measurements, drawing, and infrared absorption studies.

In general, the heptane soluble films were sticky and non-uniform when prepared by the other methods as described in Chapter III. Films of the whole and heptane insoluble polymers, prepared by methods other than described above, were porous, non-uniform, and poorly fused. The rapid quenching of the heptane soluble films in ice water was found to give coherent films that could be easily stripped from the plates.

Densities of undrawn heptane soluble and insoluble films. Table III lists the densities of the density bulbs calibrated by a flotation method at 30.4 ± 0.1° C. Duplicate determinations were made and the densities obtained were found to agree to ± 0.001 g/cm^3. Table IV lists the bulb densities with the bulb positions in the density gradient tube. These values were used to construct the density gradient tube calibration curve shown in Figure 2. The density gradient was found to be linear.

Tables V and VI give the densities of undrawn heptane soluble and insoluble films, respectively. Duplicate determinations on the same film showed a variation of ± 0.001 g/cm^3. The lowest density for a heptane soluble film was found to be 0.864 g/cm^3. The densities of the undrawn heptane soluble films were found to increase in the order of the whole polymers—105, 113, and 125. The densities of the undrawn heptane insoluble films also show increasing densities in the order of the whole polymers—105, 113, and 125.

Estimation of weight average molecular weights. The results of the weight average molecular weight estimations are shown in Table VII. These data show the heptane soluble polymers to have a low degree of polymerization with some variations between samples.

It would be expected that the extraction of the heptane soluble polymers from the whole polymers would result in increasing the weight average molecular weights of the heptane insoluble polymers. These results are indicative of an inversion of average molecular weights, since the weight average molecular weights of the heptane insoluble polymers are less than those of their corresponding whole polymers. Inversions of average molecular weights (6) have been observed for other polymer systems investigated using precipitation fractionations of polymer solutions of

TABLE III

THE DENSITIES OF THE CALIBRATED BULBS

Bulb Number	Density, g/cm^3
1	0.821
2	0.846
3	0.852
4	0.865
5	0.869
6	0.878
7	0.887
8	0.900
9	0.924
10	0.933
11	0.942
12	0.949
13	0.960

TABLE IV

THE CALIBRATION OF THE DENSITY GRADIENT TUBE

Bulb Number	Scale Reading	Density, g/cm^3
4	183	0.865
5	173	0.869
6	154	0.878
7	137	0.887
8	113	0.900
9	66	0.924
10	48	0.933
11	29	0.942

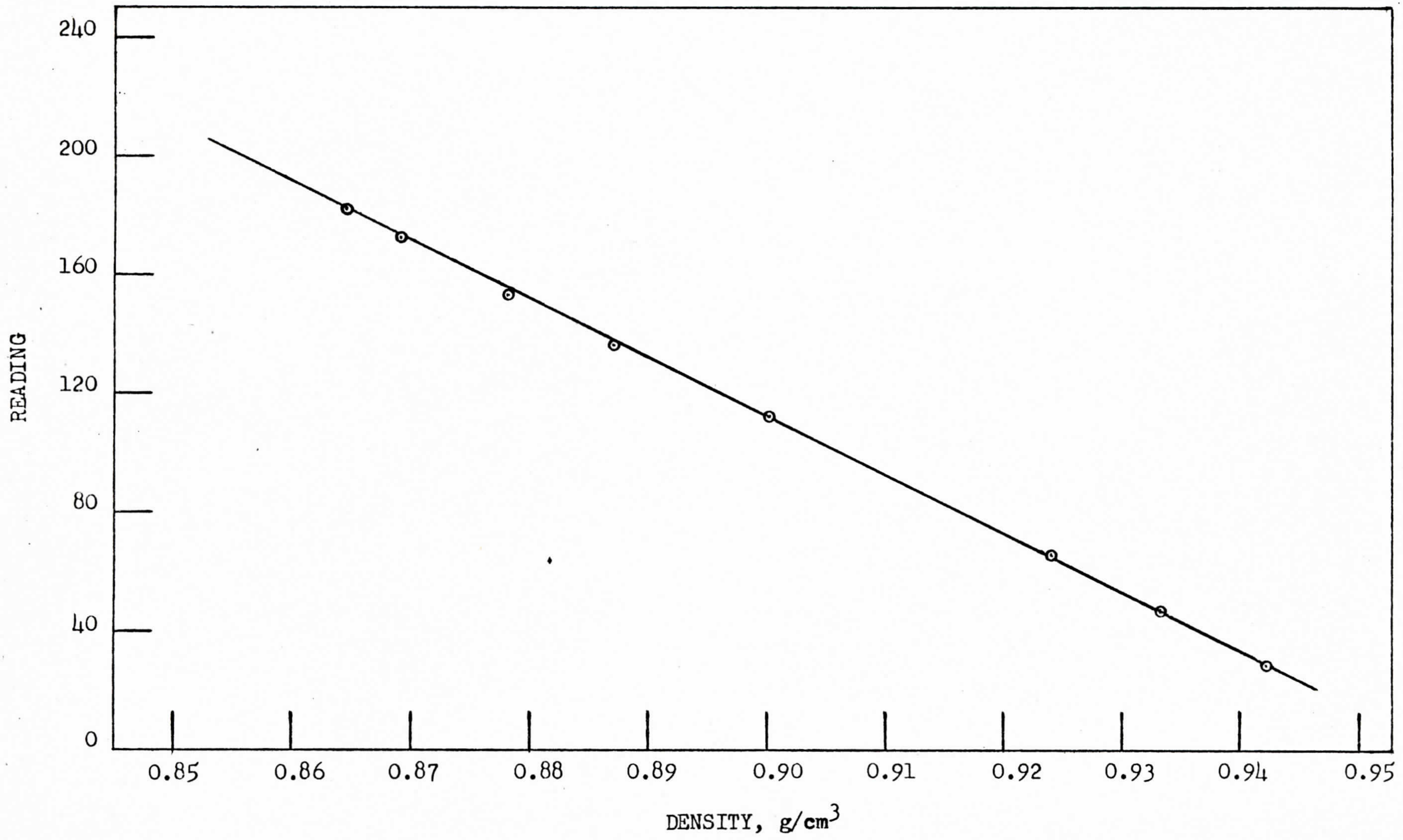


FIGURE 2

A CALIBRATION CURVE FOR THE DENSITY GRADIENT TUBE

TABLE V

THE DENSITIES OF THE HEPTANE SOLUBLE FILMS

Sample	Density, g/cm^3
105-1	0.864
105-2	0.864
105-3	0.865
105-4	0.867
105-5	0.867
105-6	0.870
105-7	0.874
113-1	0.866
113-2	0.870
113-3	0.871
113-4	0.876
113-5	0.876
113-6	0.879
113-7	0.881
125-1	0.884
125-3	0.885
125-3	0.885
125-4	0.886
125-5	0.888
125-6	0.889
125-7	0.891

TABLE VI

THE DENSITIES OF THE HEPTANE INSOLUBLE FILMS

Sample	Density, g/cm^3
105-1	0.895
105-2	0.895
105-3	0.895
105-4	0.896
105-5	0.896
105-6	0.896
105-7	0.896
113-1	0.896
113-2	0.897
113-3	0.897
113-4	0.898
113-5	0.898
113-6	0.898
113-7	0.898
125-1	0.897
125-2	0.897
125-3	0.897
125-4	0.897
125-5	0.898
125-6	0.890
125-7	0.900

TABLE VII

SPECIFIC VISCOSITIES, WEIGHT AVERAGE DEGREES OF POLYMERIZATION, AND WEIGHT AVERAGE MOLECULAR WEIGHTS FOR ESCON WHOLE POLYMERS(W), HEPTANE INSOLUBLE(R), AND HEPTANE SOLUBLE(F) FRACTIONS

Sample	η_{sp}	$\bar{P}_w$	$\bar{M}_w$
105-W	1.84	5650	237,000
105-R	1.36	4170	175,000
105-F	0.40	1230	51,700
113-W	1.87	5740	241,000
113-R	1.55	4760	200,000
113-F	0.37	1140	47,900
125-W	1.94	5950	250,000
125-R	1.91	5860	246,000
125-F	0.26	800	33,600

concentrations greater than 2% (by weight). The solutions used in this study were approximately 15% (by weight). However, the precipitation fractionations are precipitation processes, whereas, extractions as performed in this study are solution processes. The explanation for the inversion of the average molecular weights obtained in this study is not clear at present.

<u>Non-polarized infrared absorption studies</u>. Figures 3 and 4 illustrate the infrared absorption spectra of the heptane soluble and insoluble fractions, respectively. Tables VIII and IX index the absorption bands from the above spectra with respect to frequency (cm^{-1}) and band appearance. Several differences were observed upon comparing the spectra of the two fractions. The absorption bands of the spectrum of the heptane soluble fraction show increased intensities at 810, 1103, and 1265 cm^{-1} when compared to the same absorption bands of the heptane insoluble fraction. Absorption bands of the heptane soluble fraction show decreased intensities at 843, 900, 943, 1000, 1047, 1103, 1220, 1307, 1332, 2730, and 3200 cm^{-1} when compared to the heptane insoluble fraction.

The infrared absorption spectra of the heptane soluble and insoluble fractions, given in Figures 3 and 4, show a reversal of intensities for absorption bands at 809 and 843 cm^{-1}; 976 and 1000 cm^{-1}; 1000 and 1030 cm^{-1}; and 1265 and 1307 cm^{-1} for the heptane soluble fractions. These spectra also show new absorption bands at 700 and 1750 cm^{-1} and a broadening of absorption bands at 809, 1000, 1030, and 1265 cm^{-1} for the heptane soluble fraction. The 700 and 1750 cm^{-1} bands were examined further on the premise that they were solvent bands. However, a very small intensity decrease was observed upon rescanning the spectra following the heating of the same film for several hours at 110° C. If these were due to heptane, a noticeable decrease of band intensity and no change in band appearance

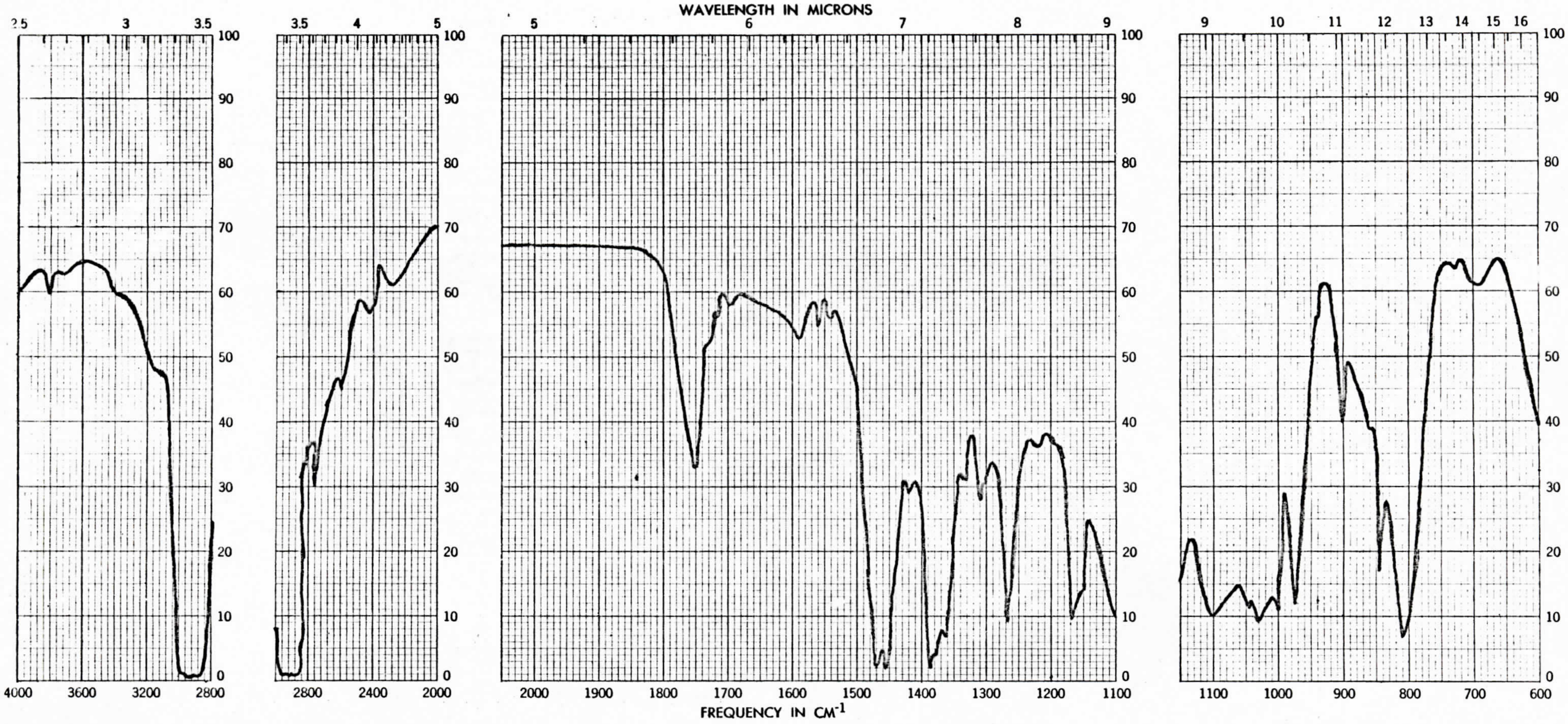


FIGURE 3

THE INFRARED SPECTRUM OF HEPTANE SOLUBLE POLYPROPYLENE

TABLE VIII

THE INFRARED SPECTRUM OF HEPTANE SOLUBLE POLYPROPYLENE

Frequency, cm^{-1}	Description
700	broad, weak
809	sharp, strong
843	very sharp
900	very sharp, moderate
943	weak shoulder
976	very sharp, strong
1000	weak
1030	weak
1047	sharp, weak
1103	broad, moderate
1154	weak shoulder
1168	sharp, moderate
1220	broad, weak
1265	very sharp, moderate
1300	weak shoulder
1307	sharp, weak
1332	weak doublet
1339	
1361	weak shoulder
1375	weak
1383	sharp, strong
1455	sharp doublet, moderate
1469	
1750	very sharp, moderate
2280	broad, weak
2440	weak
2590	weak
2730	sharp, moderate
2900	broad, strong
3150	weak
3200	weak

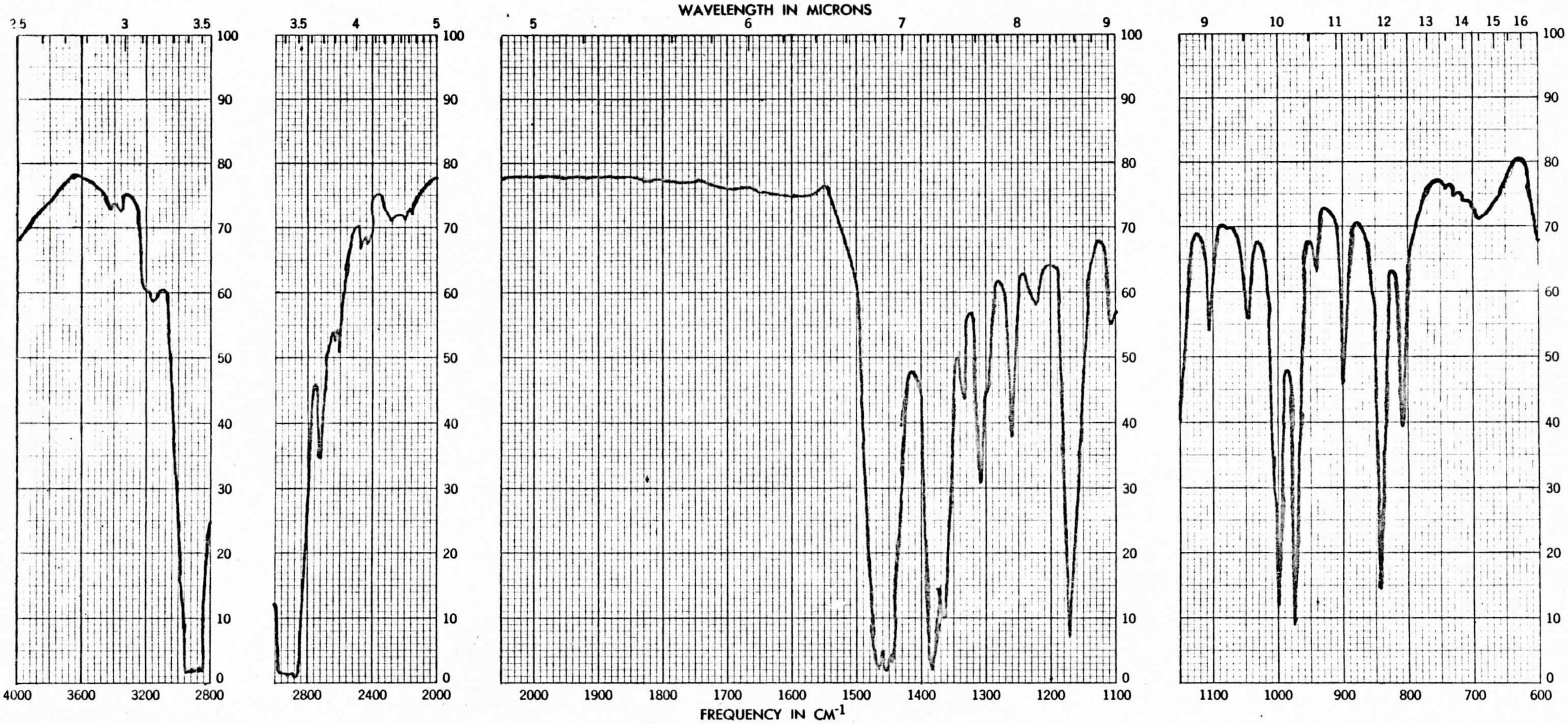


FIGURE 4

THE INFRARED SPECTRUM OF HEPTANE INSOLUBLE POLYPROPYLENE

TABLE IX

THE INFRARED SPECTRUM OF HEPTANE INSOLUBLE POLYPROPYLENE

Frequency, cm^{-1}	Description
700	broad, weak
809	sharp, moderate
843	very sharp, strong
900	sharp, moderate
943	weak
976	very sharp, strong
1000	very sharp, strong
1047	sharp, weak
1103	sharp, moderate
1158	weak shoulder
1171	very sharp, strong
1225	weak
1260	sharp, moderate
1302	weak shoulder
1309	sharp, moderate
1335	sharp, weak
1365	sharp, weak
1383	very sharp, strong
1454	very sharp doublet
1470	
2600	weak
2640	weak
2740	sharp, weak
2900	broad, strong
3175	weak
3200	weak

would occur upon heating. It was also observed, that the band became broadened upon heating. This strongly suggests that the 1750 cm^{-1} is not a solvent band. No appreciable changes in band appearance or intensity were observed for the 700 cm^{-1} band. Fair agreement was, otherwise, found with reported band assignments.

These data may be interpreted as possible evidence for a different crystalline modification of polypropylene than has previously been reported. More evidence is given by the spectra of the molten heptane soluble fraction to follow.

Determination of melting ranges of the fractions. Before infrared absorption spectra were obtained at various temperatures, the thermocouple attached to the heating cell was calibrated. Table X lists the arbitrary meter readings at various temperatures from 20 to 190° C. These values, shown graphically in Figure 5, served as a calibration curve for the thermocouple.

Figure 6 shows a spectrum of heptane insoluble film at 180° C. Table XI indexs the absorption bands with respect to frequency (cm^{-1}) and band appearance. The absorption bands of the heptane insoluble film which gave the more obvious decrease of intensity upon increasing the temperature were found at 843, 900, 1000, 1309, 1335, and 2740 cm^{-1}. The same was found to be true for the same absorption bands of the heptane soluble film, except a smaller change of intensity was observed.

The effects of temperature upon the absorbance of several absorption bands for a film of the heptane soluble fraction are given in Table XII and are shown graphically in Figure 7 for the absorption band at 900 cm^{-1}. Temperature effects upon the absorbance of several absorption bands for a film of the heptane insoluble fraction are given in Table XIII and are shown graphically in Figure 8 for the absorption band at 843 cm^{-1}. These

TABLE X

THE CALIBRATION OF THE THERMOCOUPLE

Observation	Meter Reading	Temperature, °C
1	0	20
2	4.0	30
3	8.0	40
4	12.0	50
5	16.0	60
6	20.5	70
7	24.5	80
8	28.5	90
9	32.5	100
10	36.5	110
11	40.5	120
12	44.5	130
13	48.5	140
14	53.0	150
15	57.0	160
16	61.0	170
17	65.0	180
18	69.0	190

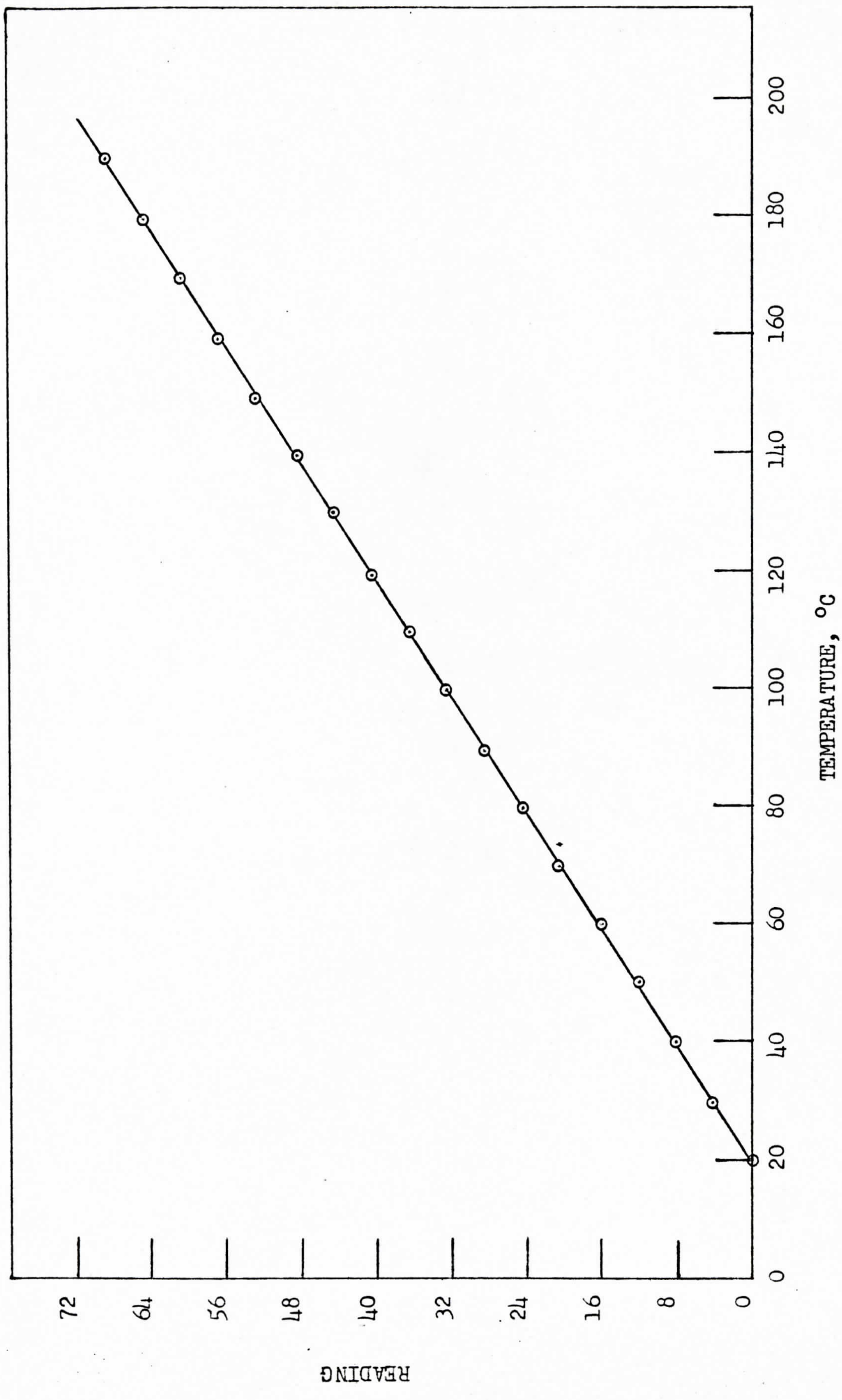


FIGURE 5

A CALIBRATION CURVE FOR THE THERMOCOUPLE

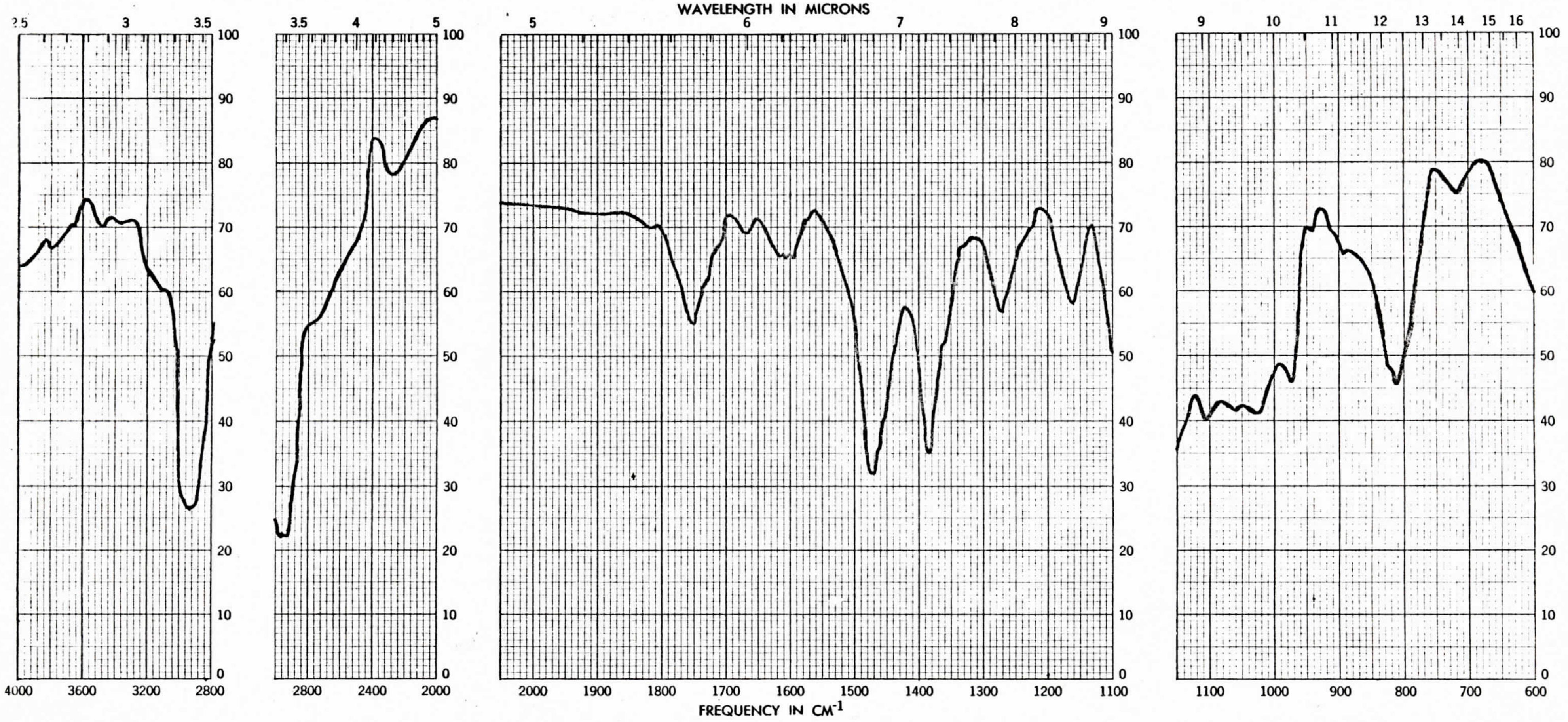


FIGURE 6

THE INFRARED SPECTRUM OF A HEPTANE INSOLUBLE POLYPROPYLENE FILM AT 180°C

TABLE XI

THE INFRARED SPECTRUM OF A HEPTANE SOLUBLE FILM AT 180°C

Frequency, cm^{-1}	Description
710	broad, weak
813	broad, moderate
820	weak shoulder
840	very weak shoulder
895	very weak
935	very weak
976	weak shoulder
980	weak
1025	broad, weak
1105	broad, weak
1160	broad, moderate
1228	very weak shoulder
1268	broad, moderate
1303	very weak shoulder
1335	very weak shoulder
1362	very weak shoulder
1385	sharp, strong
1438	very weak shoulder
1447	very weak shoulder
1458	shoulder
1468	broad, strong
1600	broad, moderate
1675	broad, weak
1719	weak shoulder
1735	weak shoulder
1750	broad, moderate
2280	broad, moderate
2530	shoulder
2740	very weak
2940	broad, strong
3140	weak shoulder

TABLE XII

THE RELATIONSHIP OF ABSORBANCE AND TEMPERATURE FOR AN ESCON-113 HEPTANE SOLUBLE FILM

Temperature, °C	Absorbance			
	809 cm^{-1}	843 cm^{-1}	900 cm^{-1}	1000 cm^{-1}
35	0.38	0.22	0.08	0.26
50	0.36	0.22	0.08	0.23
70	0.35	0.21	0.07	0.23
90	0.31	0.19	0.05	0.20
100	0.31	0.18	0.04	0.18
120	0.28	0.14	0.03	0.15
140	0.23	0.12	0.03	0.12
160	0.20	0.10	0.03	0.10
180	0.16	0.08	0.03	0.07

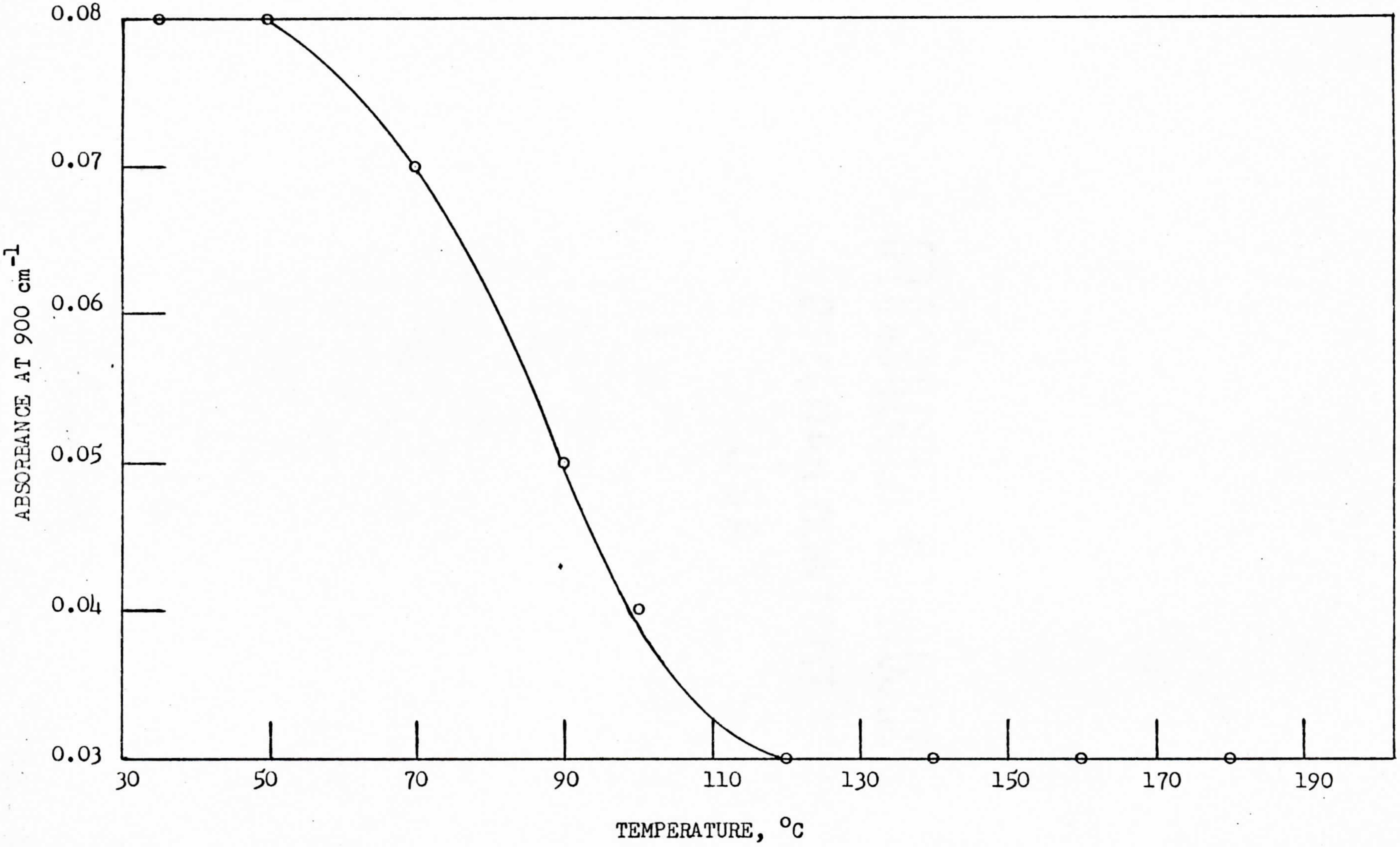


FIGURE 7

THE RELATIONSHIP OF ABSORBANCE AT 900 cm^{-1} AND TEMPERATURE FOR AN ESCON-113 HEPTANE SOLUBLE FILM

TABLE XIII

THE RELATIONSHIP OF ABSORBANCE AND TEMPERATURE FOR AN ESCON-113 HEPTANE INSOLUBLE FILM

Temperature, °C	Absorbance			
	810 cm^{-1}	843 cm^{-1}	900 cm^{-1}	1000 cm^{-1}
50	0.35	0.52	0.23	0.66
70	0.33	0.51	0.21	0.63
90	0.31	0.48	0.18	0.58
110	0.29	0.44	0.17	0.52
130	0.27	0.38	0.15	0.44
150	0.26	0.27	0.13	0.18
160	0.12	0.13	0.09	0.13
170	0.11	0.11	0.05	0.10
190	0.10	0.11	0.05	0.10

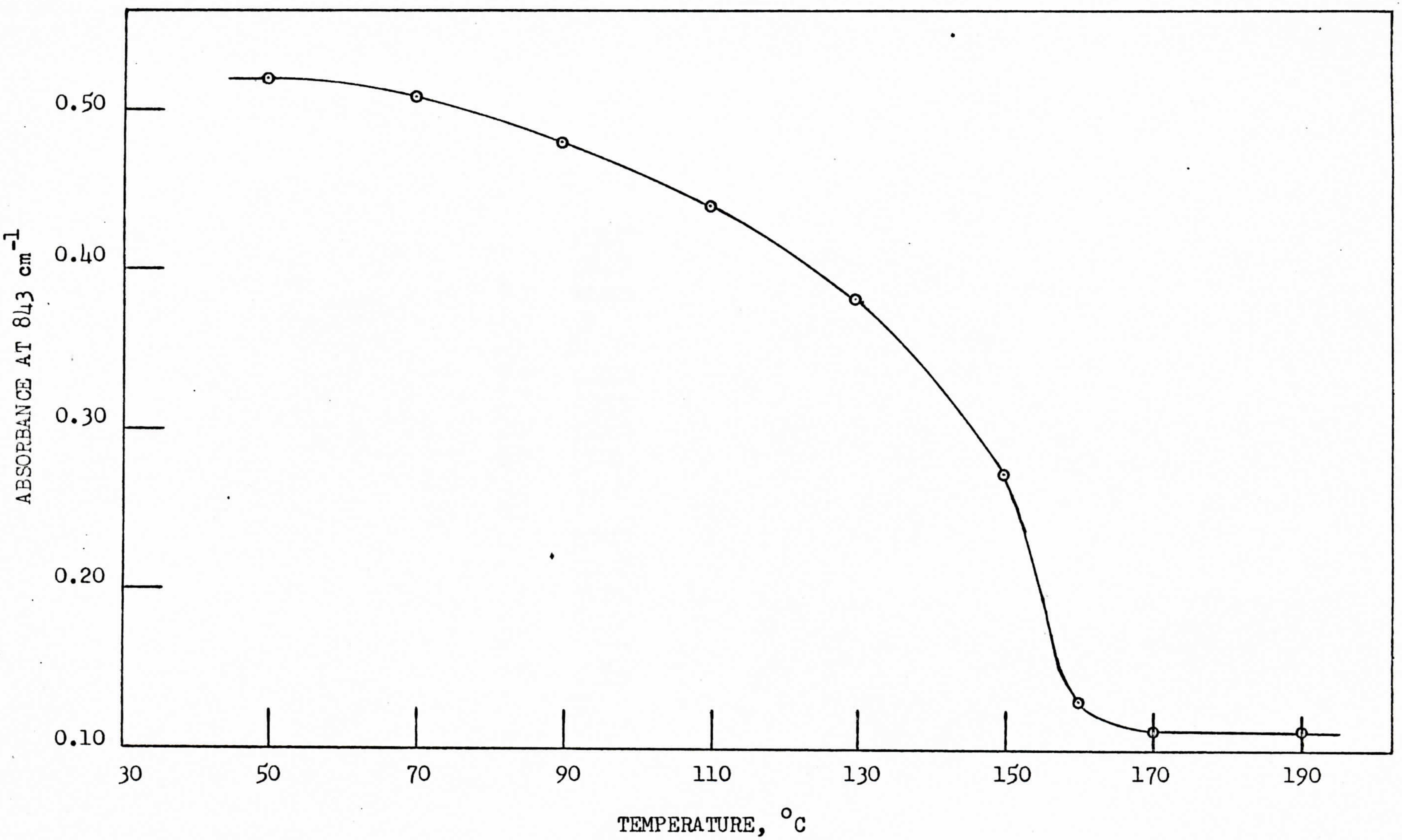


FIGURE 8

THE RELATIONSHIP OF ABSORBANCE AT 843 cm^{-1} AND TEMPERATURE FOR AN ESCON-113 HEPTANE INSOLUBLE FILM data indicate that the heptane soluble fraction was completely molten when a temperature of 120° C. was reached, and the heptane insoluble fraction was completely molten when a temperature of 170° C. was reached. It was found that the use of an internal thickness standard as suggested by Heinen (4) was not necessary in this study.

Upon comparison of the spectra of the heptane soluble (Figure 3) and heptane insoluble films (Figure 4) at room temperature with the spectra of the same films at elevated temperatures, it was observed that the 1750 cm^{-1} absorption band appears in the spectra of the heptane soluble film at all temperatures from 20 to 190° C. The same absorption band appears in the spectra of the heptane insoluble film at temperatures above its melting range--above 170° C. The 700 cm^{-1} absorption band appeared in all spectra of the heptane soluble and insoluble fractions at all temperatures from 20 to 190° C. Both of these absorption bands have been reported in similar studies (5). The 700 cm^{-1} absorption band was assigned to the presence of short chains in the sample and the 1750 cm^{-1} absorption band, to impurities in the sample from the extraction process, oxidation products involving the $-\underset{|}{\overset{|}{C}}{=}O$ group, or other sources. It might be noted that $-\underset{|}{C}{=}O$ absorption bands have been reported from oxidation studies of polypropylene (11) near 1700 cm^{-1}, but none as sharp as the 1750 cm^{-1} band in this study.

These data are proposed as possible evidence for a different crystalline modification for polypropylene than has been previously reported.

II. CHARACTERIZATION OF DRAWN HEPTANE SOLUBLE AND INSOLUBLE FILMS

Drawing of films. Because films of the heptane soluble fraction could not be drawn, only films of the heptane insoluble fraction were drawn to give various draw ratios. It was found in this study that heptane soluble films could not be drawn even at temperatures very close to the melting temperature of the films. The films sheared with the slightest amount of drawing. Heptane insoluble films were drawn to give draw ratios from 0 to approximately 7.00 as listed in Tables XVI, XVII, and XVIII. A draw ratio of approximately 7.00 was found to be the maximum draw ratio, which could be obtained before shearing or uneven stretching occurred. It was observed that the drawing rate determined the clarity and uniformity of the drawn film. Greater drawing rates produced films of satisfactory properties for polarized infrared absorption studies.

All drawn films were observed to relax or shrink upon the release of the drawing force. However, the extent of relaxation was observed to be no more than approximately 20% of the length before drawing. It was suggested that some relaxation could have occurred after ceasing to observe the film once drawing had been achieved. This residual relaxation was examined by measuring the length after drawing and several hours following the drawing process. No appreciable relaxation was observed.

Polarized infrared absorption studies. Figures 9 and 10 show the parallel and perpendicular polarized spectra for an Escon-105 heptane insoluble film of draw ratio, 6.70. The absorption bands for the above film are indexed with respect to frequency (cm^{-1}), relative intensity, and polarization effect in Table XIV. Dichroic ratios and average orientation angles were calculated from the above mentioned spectra. Table XV gives the dichroic ratios and average orientation angles for the absorption bands, whose group assignments were reported by Liang and Pearson (9).

Comparison of the frequencies and polarization effects previously reported and those obtained in this study show fairly good agreement,

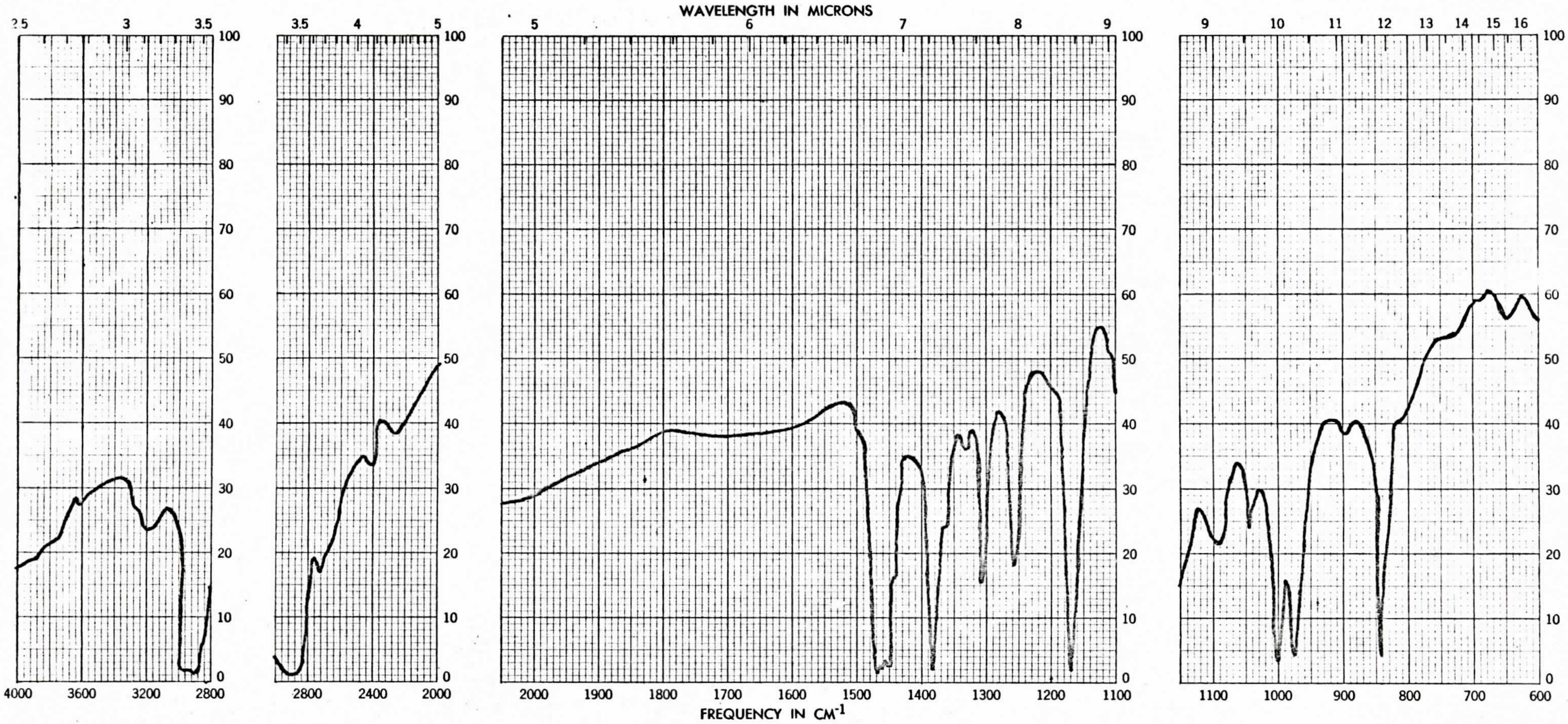


FIGURE 9

THE POLARIZED INFRARED SPECTRUM OF A DRAWN HEPTANE INSOLUBLE POLYPROPYLENE FILM

(DRAW DIRECTION PARALLEL TO ELECTRIC VECTOR OF POLARIZED RADIATION)

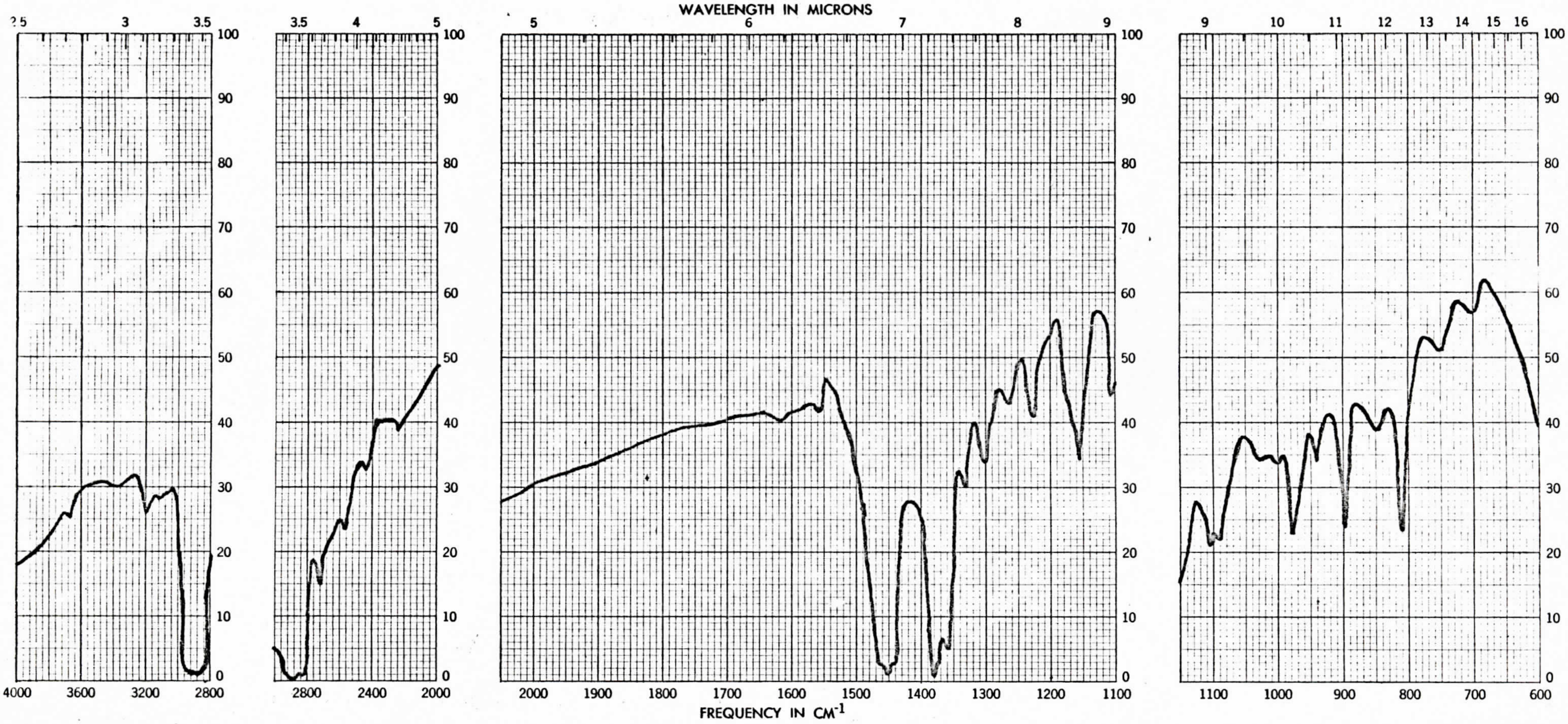


FIGURE 10

THE POLARIZED INFRARED SPECTRUM OF A DRAWN HEPTANE INSOLUBLE POLYPROPYLENE FILM

(DRAW DIRECTION PERPENDICULAR TO ELECTRIC VECTOR OF POLARIZED RADIATION)

TABLE XIV

THE POLARIZED INFRARED SPECTRUM OF HEPTANE INSOLUBLE POLYPROPYLENE

Frequency, cm^{-1}	Relative Intensity	Polarization
700	weak	⊥
750	weak	⊥
810	sharp	⊥
843	sharp	∥
900	sharp	⊥
942	weak	⊥
976	sharp	∥
1000	sharp	∥
1046	moderate	∥
1090	weak	⊥
1103	weak	⊥
1158	sharp	⊥
1171	sharp	∥
1222	moderate	⊥
1260	sharp	∥
1300	moderate	⊥
1308	sharp	∥
1332	weak	⊥
1360	sharp	⊥
1382	sharp	⊥
1441	shoulder	⊥
1452	sharp	⊥
1466	sharp	∥
2835	sharp	∥
2855	sharp	∥
2880	sharp	∥
2910	very sharp	∥
2920	very sharp	∥
2930	very sharp	∥
2950	very sharp	⊥
2960	very sharp	∥

TABLE XV

FREQUENCIES, DICHROIC RATIOS, AVERAGE ORIENTATION ANGLES, POLARIZATION EFFECTS, AND GROUP INTERPRETATIONS FOR AN ESCON-105 HEPTANE INSOLUBLE FILM DRAW RATIO, 6.70

Frequency, cm^{-1}	R	θ	Polarization	Interpretation
810	0.30	21	⊥	CH_2 rocking, C-C stretching, CH_3 wagging and rocking
843	8.31	26	||	
900	0.22	19	⊥	
942	0.21	18	⊥	
976	3.62	37	||	
1000	11.80	22	||	
1046	6.08	30	||	
1103	0.55	28	⊥	
1171	6.33	29	||	
1222	0.35	23	⊥	CH_2 twisting and CH bending
1260	4.66	33	||	
1308	2.68	41	||	CH_2 wagging and CH bending
1332	0.62	29	⊥	
1360	0.32	22	⊥	
1382	0.91	34	⊥	Sym. CH_3 bending
1452	0.85	33	⊥	CH_2 bending and anti-sym. CH_3 bending
1466	1.15	53	||	

except for bands at 700, 750, 810, and 1090 cm^{-1} which were not reported, but were found in this study. Also some disagreement with the reported polarization effects was found in this study for the 1452, 1466, 2855, 2880, 2920, and 2930 cm^{-1} absorption bands. This study showed a reversal of polarization effects for the absorption bands at 1452, 1466, 2855, 2880, and 2920 cm^{-1}, while no assignment was given for the absorption band at 2930 cm^{-1}. This study observed the 2930 cm^{-1} absorption band to be parallel. The above disagreements may not be serious because of the relatively low intensities of the absorption bands mentioned above with the exception of bands found at 700 and 1750 cm^{-1}. These bands have been discussed in previous results.

Densities and percentage crystallinities of the drawn heptane insoluble films. The densities of the drawn heptane insoluble films were obtained several hours after being drawn. Percentage crystallinities were calculated, as described in Chapter III, from the obtained densities and are listed along with the densities in Tables XVI, XVII, and XVIII. Densities were found to be reproducible to ± 0.001 g/cm^3 for density samples of the same film which corresponds to a reproducibility of ± 1.4% for percentage crystallinities.

Correlation of percentage crystallinity and draw ratio for drawn films of the heptane insoluble fractions. Tables XVI, XVII, and XVIII list the calculated percentage crystallinities and the measured draw ratios for films of the heptane insoluble fractions of Escon-105, 113, and 125, respectively. Since no correlation of percentage crystallinity and draw ratio could be found in this study, only one attempt at the correlation of these two variables, that for drawn films of heptane insoluble Escon-125, is shown in Figure 11.

TABLE XVI

DRAW RATIOS, DENSITIES, AND PERCENTAGE CRYSTALLINITIES OF ESCON-125 HEPTANE INSOLUBLE FILMS

Sample	Draw Ratio	Density, g/cm^3	% X
1	2.10	0.896	46.4
2	2.40	0.897	47.8
3	2.90	0.898	49.2
4	3.10	0.902	54.8
5	3.30	0.899	50.6
6	3.50	0.897	47.8
7	3.50	0.898	49.2
8	4.20	0.897	47.8
9	4.30	0.897	47.8
10	4.70	0.899	50.6
11	5.10	0.900	52.0
12	5.30	0.900	52.0
13	5.40	0.896	46.4
14	5.60	0.902	54.8
15	5.60	0.900	52.0
16	6.10	0.897	47.8
17	6.30	0.900	52.0

TABLE XVII

DRAW RATIOS, DENSITIES, AND PERCENTAGE CRYSTALLINITIES OF ESCON-113 HEPTANE INSOLUBLE FILMS

Sample	Draw Ratio	Density, g/cm^3	% X
1	1.00	0.899	50.6
2	1.40	0.898	49.2
3	1.40	0.897	47.8
4	1.70	0.895	45.0
5	1.80	0.898	49.2
6	2.00	0.896	46.4
7	2.20	0.897	47.8
8	2.40	0.896	46.4
9	2.50	0.898	49.2
10	2.50	0.899	50.6
11	2.60	0.896	46.4
12	2.80	0.898	49.2
13	3.50	0.897	47.8
14	3.50	0.896	46.4
15	3.60	0.899	50.6
16	4.00	0.898	49.2
17	4.90	0.896	46.4
18	5.10	0.896	46.4
19	5.30	0.898	49.2
20	6.00	0.898	49.2
21	6.60	0.897	47.8

TABLE XVIII

DRAW RATIOS, DENSITIES, AND PERCENTAGE CRYSTALLINITIES OF ESCON-105 HEPTANE INSOLUBLE FILMS

Sample	Draw Ratio	Density, g/cm^3	% X
1	1.60	0.896	46.4
2	1.80	0.896	46.4
3	2.20	0.897	47.8
4	2.40	0.895	45.0
5	2.50	0.895	45.0
6	2.60	0.896	46.4
7	2.80	0.896	46.4
8	3.40	0.896	46.4
9	3.80	0.895	45.0
10	3.80	0.898	49.2
11	4.10	0.896	46.4
12	4.90	0.896	46.4
13	4.90	0.895	45.0
14	5.00	0.894	43.6
15	5.00	0.894	43.6
16	5.10	0.896	46.4
17	5.70	0.896	46.4
18	5.90	0.896	46.4
19	6.30	0.895	45.0
20	6.70	0.895	45.0
21	6.70	0.898	49.2

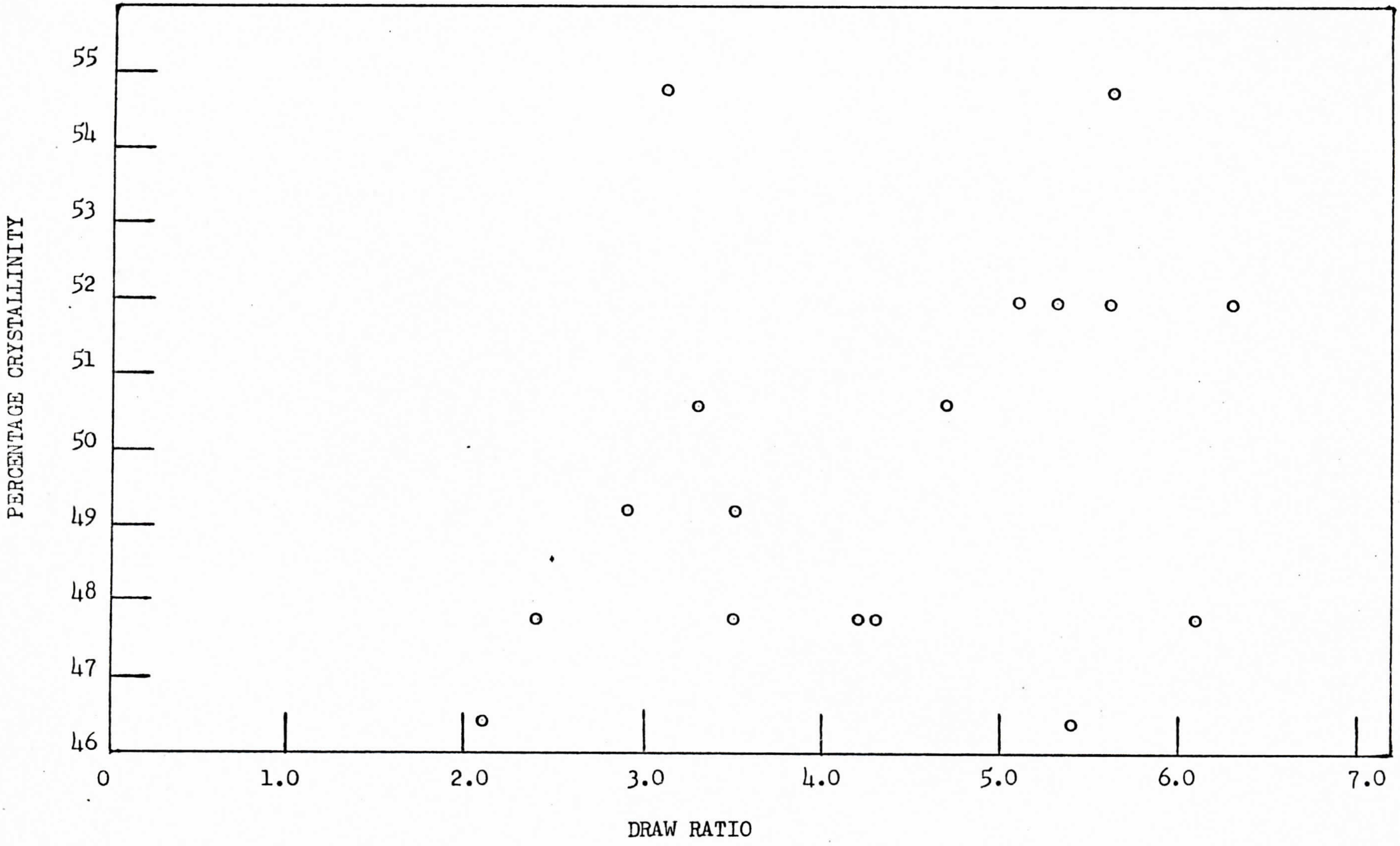


FIGURE 11

THE RELATIONSHIP OF PERCENTAGE CRYSTALLINITY AND DRAW RATIO FOR THE ESCON-125 HEPTANE INSOLUBLE FILMS

Correlation of percentage crystallinity and average orientation angle for drawn films of the heptane insoluble fractions. Tables XIX, XX, and XXI list the percentage crystallinities and average orientation angles for films of the heptane insoluble fractions of Escon-105, 113, and 125, respectively. Average orientation angles were calculated from dichroic ratios of the polarized infrared absorption bands at 840, 1255, and 1303 cm^{-1}. Since no correlation of percentage crystallinity and average orientation angle could be found in this study, only one attempt at the correlation of these two variables, that for drawn films of heptane insoluble Escon-125, is shown in Figure 12.

Several reasons may be proposed for the lack of correlation of percentage crystallinity, draw ratio, and average orientation angle. Among these several reasons are (1) accuracy of density determination, (2) accuracy of draw ratios, (3) high crystallinity of the heptane insoluble polymers, (4) variation of orientation during film preparation, and (5) accuracy of dichroic ratios.

Of the above reasons, two merit consideration relative to this study. They are the high crystallinity of the heptane insoluble polymers and the accuracy of dichroic ratios. It may be hypothesized from these findings that the crystallinity of the heptane insoluble fraction could not be increased appreciably by drawing, since a high crystallinity of the chain molecules has been achieved upon the removal of the low D. P. material. Also since there were thickness variations of each film scanned by polarized infrared radiation, the internal thickness standards used would not correct for thickness variations only, because the thickness standards were found to also exhibit some dichroism.

TABLE XIX

PERCENTAGE CRYSTALLINITIES, AND AVERAGE ORIENTATION ANGLES AT 843, 1260, AND 1308 cm^{-1} CORRECTED FOR THICKNESS AS INDICATED AT 976 AND 1171 cm^{-1} FOR ESCON-125 HEPTANE INSOLUBLE FILMS

Sample	% X	Average Orientation Angle					
		$\frac{843}{976}$	$\frac{1260}{976}$	$\frac{1308}{976}$	$\frac{843}{1171}$	$\frac{1260}{1171}$	$\frac{1308}{1171}$
1	46.4	33	44	54	38	49	31
2	49.2	29	43	54	31	47	33
3	47.8	24	36	52	27	39	35
4	47.8	22	44	52	24	47	23
5	50.6	28	42	34	30	44	31
6	52.0	36	39	32	40	35	28
7	46.4	31	47	31	33	49	29
8	52.0	28	41	49	32	45	53
9	47.8	32	41	34	32	43	33
10	52.0	30	41	32	33	45	28

TABLE XX

PERCENTAGE CRYSTALLINITIES, AND AVERAGE ORIENTATION ANGLES AT 843, 1260, AND 1308 cm^{-1} CORRECTED FOR THICKNESS AS INDICATED AT 976 AND 1711 cm^{-1} FOR ESCON-113 HEPTANE INSOLUBLE FILMS

Sample	% X	Average Orientation Angle					
		$\frac{843}{976}$	$\frac{1260}{976}$	$\frac{1308}{976}$	$\frac{843}{1171}$	$\frac{1260}{1171}$	$\frac{1308}{1171}$
1	50.6	41	48	33	44	53	29
2	47.8	38	52	34	42	34	29
3	49.2	29	42	52	31	37	54
4	50.6	26	40	53	31	47	31
5	50.6	23	31	53	25	33	54
6	49.2	24	41	52	29	26	33
7	46.4	23	49	33	27	53	29
8	49.2	28	37	53	29	51	35
9	49.2	33	42	32	38	47	27
10	47.8	26	43	34	29	47	30

TABLE XXI

PERCENTAGE CRYSTALLINITIES, AND AVERAGE ORIENTATION ANGLES AT 843, 1260, AND 1308 cm^{-1} CORRECTED FOR THICKNESS AS INDICATED AT 976 AND 1171 cm^{-1} FOR ESCON-105 HEPTANE INSOLUBLE FILMS

Sample	% X	Average Orientation Angle					
		$\frac{843}{976}$	$\frac{1260}{976}$	$\frac{1308}{976}$	$\frac{843}{1171}$	$\frac{1260}{1171}$	$\frac{1308}{1171}$
1	46.4	37	45	33	31	49	30
2	45.0	37	45	33	42	49	30
3	45.0	37	50	34	44	34	28
4	46.4	34	49	32	39	54	28
5	46.4	24	45	35	27	50	31
6	45.0	35	47	31	37	49	30
7	46.4	31	39	34	34	42	31
8	43.6	42	31	26	44	30	24
9	43.6	31	44	35	35	49	31
10	46.4	22	54	34	26	31	29
11	45.0	20	39	53	22	43	33
12	45.0	30	43	35	21	32	44

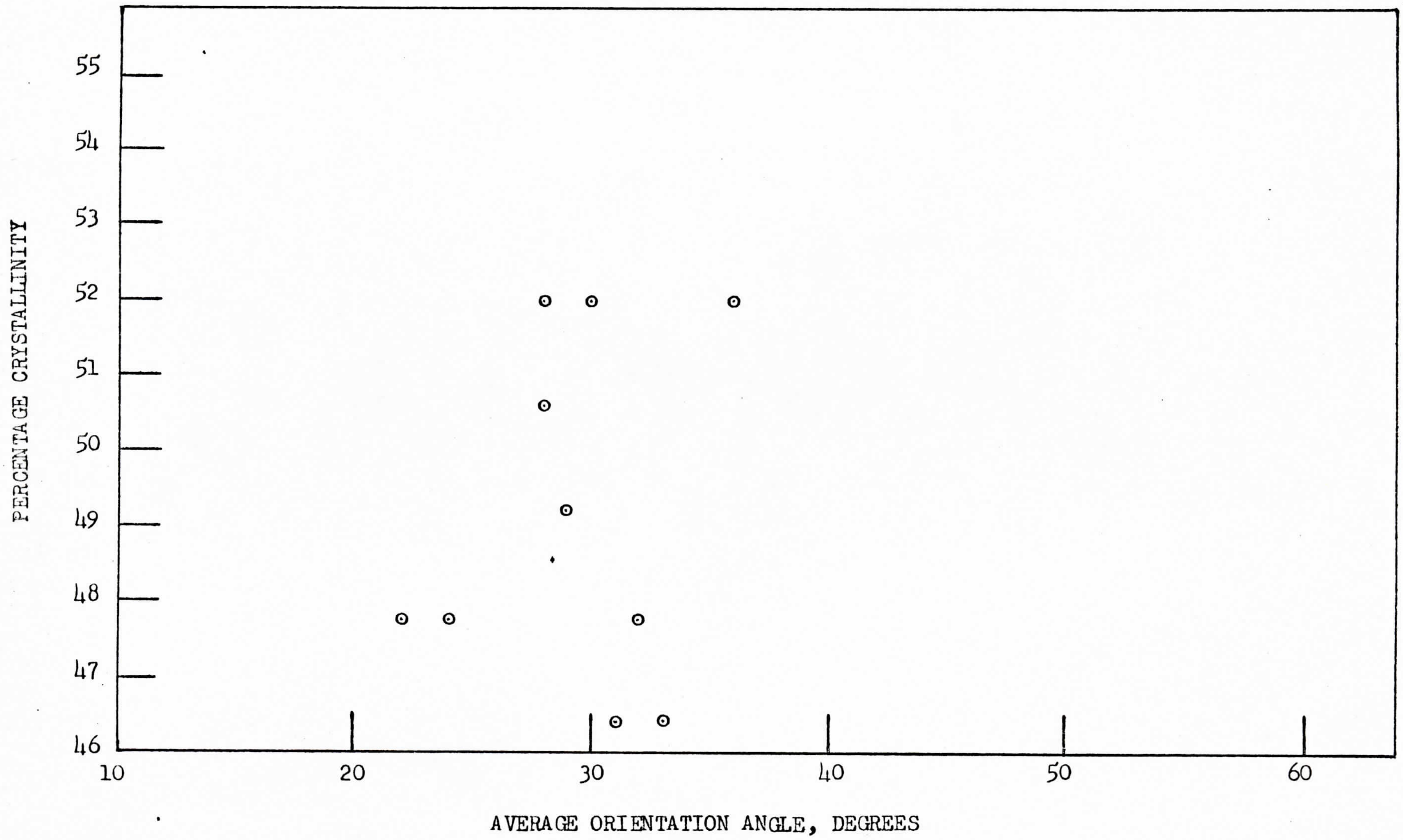


FIGURE 12

THE RELATIONSHIP OF PERCENTAGE CRYSTALLINITY AND AVERAGE ORIENTATION ANGLE FOR THE ESCON-125 HEPTANE INSOLUBLE FILMS

CHAPTER V

CONCLUSIONS

This study concludes that

1. A different crystalline modification for stereoregular polypropylene might be suggested.
2. No correlation of percentage crystallinity, draw ratio, and average orientation angle could be found for drawn stereoregular polypropylene samples used in this study.
3. Drawing increases the crystallite orientation.

CHAPTER VI

SUGGESTIONS FOR FURTHER STUDY

The results of this investigation suggest several ideas for further study.

X-ray studies of polypropylene should be made in an attempt to verify the possibility of the existence of a new crystalline structure. If a new structure does exist, it should be characterized. If a new structure does not exist, an explanation of the infrared evidence might be suggested.

The low and high molecular weight fractions of stereoregular polypropylenes of varying crystallinities should be investigated in an attempt to find a correlation of crystallinity and orientation parameters. It would be especially interesting and highly valuable to find a correlation of crystallinity and orientation parameters for the low molecular weight stereoregular polypropylenes.

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