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AN INVESTIGATION BY INFRARED SPECTROSCOPY  
OF THE CRYSTALLINE ORDER 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  
Earl Don Loos, Jr.  
August, 1965

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## CHAPTER I

### INTRODUCTION AND THE PROBLEM

#### I. INTRODUCTION

Polypropylene, as with many other polymer systems, serves as the basis for the production of certain molded articles and textiles of considerable commercial importance. It is well known that the mechanical and physical properties of these commercial items are intimately related to the particular physical structure of the polymer and that the physical structure is in turn reflected by the crystalline order of the various polymer molecules.

#### II. THE PROBLEM

Statement of the problem. It was the purpose of this study to prepare films of polypropylene polymer representing a wide density range, to investigate the infrared spectrum of polypropylene as a function of temperature, and to devise a method for correlating the specific volumes, a crystallinity dependent parameter, of polypropylene films with the intensities of certain crystalline sensitive absorption bands found in the infrared spectra of the films.

Importance of the problem. Many of the operations used in the fabrication of molded and textile articles from

polypropylene involve after-mechanical and thermal treatments. Such treatments are designed to modify the mechanical and physical properties in such a way that the final article will possess desirable characteristics. These modifications find their explanation in changes in the structural elements of the polymer; hence, the measurement of the degree of crystallinity in the polymeric system is of prime importance.

## CHAPTER II

### REVIEW OF THE LITERATURE

#### I. CHARACTERISTIC PREPARATION OF STEREOREGULAR POLYPROPYLENE

Stereoregular polypropylene is a vinyl type, high polymer prepared by the polymerization of propylene with the aid of a catalyst obtained by mixing a catalytic heavy metal compound, such as titanium tetrachloride, and a catalytic metal alkyl compound, such as aluminum triethyl, in a solvent inert to the polymer, such as a saturated aliphatic hydrocarbon. Polymerization is effected by heating the mixture (9)(14).

#### II. PHYSICAL STRUCTURE OF POLYPROPYLENE

The physical structure of stereoregular polypropylene is considered to be the conventional two phase order-disorder structure. In this structure the chain molecules align themselves with respect to one another into a three dimensionally ordered structure over certain areas, referred to as the crystalline regions of the polymer. In other regions, the amorphous regions, no alignment occurs and complete disorder exists. The physical properties are, therefore, interpreted in accordance with this two phase order-disorder system. For

example, drawing and annealing treatments tend to augment the crystalline regions so as to increase the crystallinity of the polymer. On the other hand, rapid quenching tends to decrease the crystalline areas and, thus, increase the amorphous areas of the polymer.

From x-ray diffraction results, Natta and Corradini (10) found that stereoregular polypropylene contained both crystalline and amorphous regions. However, after extracting the polypropylene, x-ray data showed the ether and heptane insoluble fraction to be highly crystalline having chain molecules with high regularity of structure and the acetone insoluble, ether soluble fraction to be amorphous. The resulting crystalline structure, termed isotactic, is depicted in Figure 1. Natta and Corradini (11) proposed a crystal unit cell for the isotactic polypropylene which was monoclinic and contained twelve monomeric units. The calculation of the density from this cell gives a value of 0.936 g/cc for the completely crystalline polypropylene as compared to the density of 0.850 g/cc extrapolated for the amorphous polypropylene (10)(13).

### III. STUDIES OF THE BAND ASSIGNMENTS FOR POLYPROPYLENE INFRARED SPECTRA

Numerous studies have been made concerning the infrared spectra of polypropylene, and one of the reasons for these

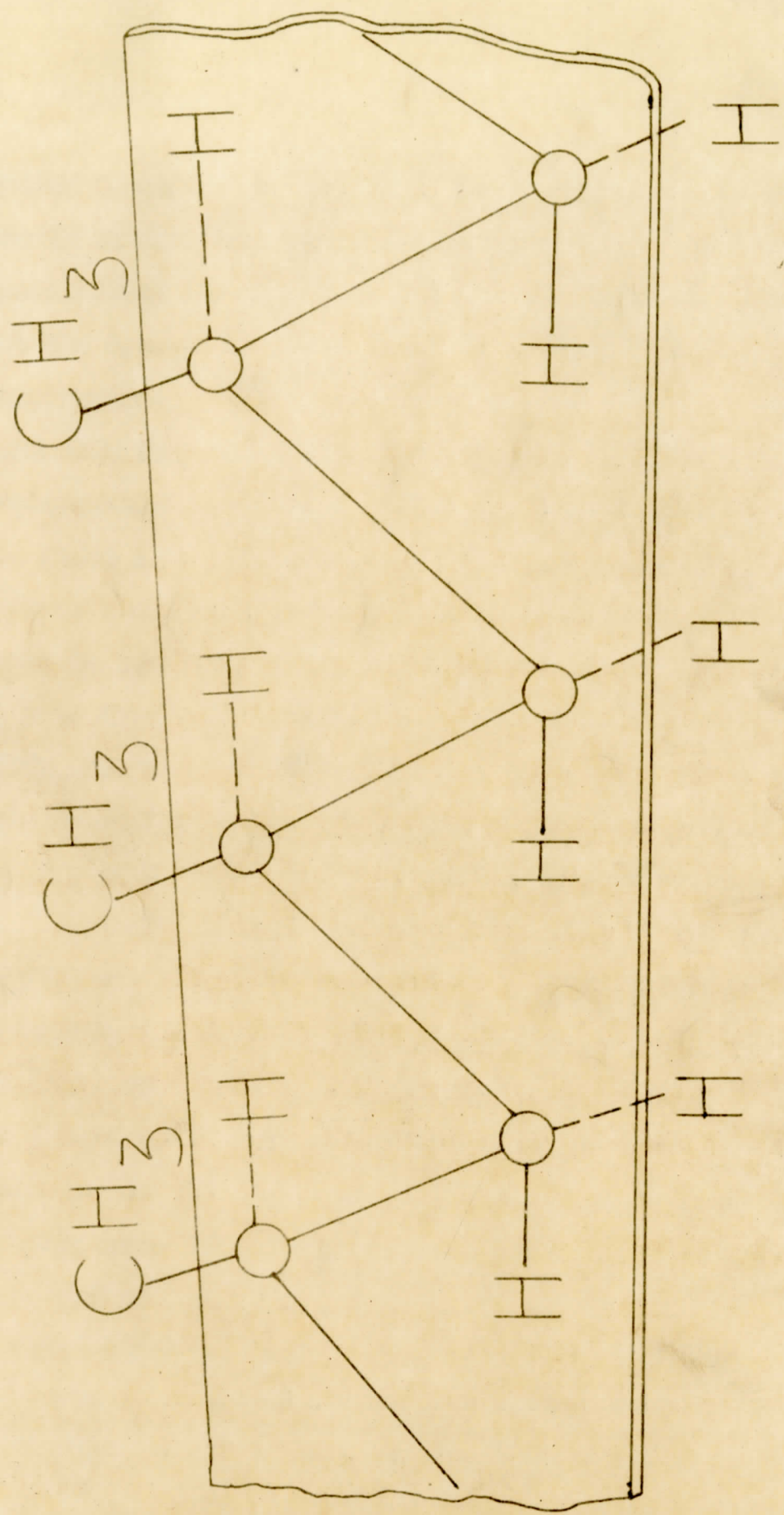


FIGURE I  
STRUCTURE OF CRYSTALLINE (ISOTACTIC) POLYPROPYLENE



studies is reflected by Zbinden's (20) statement, "Polypropylene is probably the polymer that shows the most striking crystallinity effects in the infrared spectrum." It is true that the spectrum of a stereoregular or highly crystalline polypropylene sample is markedly different in the molten state than in the solid state as was shown by a number of investigations (1)(3)(5)(8)(16)(18). All of these studies have shown a remarkable disappearance in certain infrared bands as a stereoregular or highly crystalline polypropylene sample is heated to melt temperatures. The most striking of the band disappearances occurs with the rather sharp and highly absorbing  $809\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$ ,  $900\text{ cm}^{-1}$ , and  $1000\text{ cm}^{-1}$  bands found in infrared spectra of stereoregular and highly crystalline polypropylenes at room temperatures.

Although, due to instrument resolution and other factors, the bands indexed by the various investigators are not exactly the same in all cases for the crystalline, amorphous, and molten polypropylenes, they are seldom more than 5 wave numbers out of agreement. The bands as indexed by the various investigators (1)(8)(9)(19) may, therefore, be fairly accurately summarized. For crystalline polypropylene the more important infrared bands are found at about the following wavenumbers ( $\text{cm}^{-1}$ ):

809	976	1158	1306	1462	2980
843	1000	1170	1312	2640	3152
900	1048	1222	1366	2730	3200
943	1105	1262	1379	2845.	

The more prominent infrared bands found in the spectra of molten polypropylene samples occur at about the following wavenumbers ( $\text{cm}^{-1}$ ):

810	1002	1258	1377
900	1153	1333	1458.
974	1170	1366	

Most of the bands are weaker and broader than in the solid polymer; however, the  $1458 \text{ cm}^{-1}$ ,  $1377 \text{ cm}^{-1}$ ,  $1170 \text{ cm}^{-1}$ , and  $974 \text{ cm}^{-1}$  bands remain quite strong in the molten sample. The bands found in the amorphous polypropylene closely parallel those found in the molten crystalline polymer.

#### IV. CRYSTALLINITY MEASUREMENTS OF POLYPROPYLENE

##### X-ray Determination

Natta, Corradini, and Cesare (12) developed a quantitative determination of polypropylene crystallinity, using x-ray data. The relationship found between the diffracted intensity of the crystalline portion of the sample and the sum of that in the crystalline portion and that of the amorphous portion was used to establish the relationship:

$$\text{crystallinity} = \frac{I_c}{I_c + KI_a}$$

where  $I_c$  is the corrected diffracted intensity of the crystalline part within a certain angular interval,  $I_a$  is the corrected diffracted intensity of the amorphous portion

in an angular interval, and K is a constant taken as unity in this determination. Quynn et al. (16) repeated this determination with satisfactory results.

#### Density Determination

Quynn et al. (16) calculated the per cent crystallinity (by weight) from density determinations carried out in an ethanol/water density gradient tube. The calculations of crystallinities were based on Natta's figures for the density of completely amorphous and completely crystalline polypropylene.

#### Infrared Determination

Several infrared methods of determining the crystallinity of polypropylene have been developed; however, there has been some general lack of agreement as to the best method. Although all of the methods entail the use of absorbance ratios of one type or another, the ratios vary from one investigator to the next.

One of the first infrared approaches to polypropylene crystallinity measurements was done by Heinen (6). He selected the  $846 \text{ cm}^{-1} / 1171 \text{ cm}^{-1}$  absorbance ratio as his measure of polypropylene crystallinities. He based his selection of this ratio on infrared studies in which the ratio decreased as a function of increasing temperatures. Because of the shoulder band associated with the  $1171 \text{ cm}^{-1}$  infrared

band, Luongo (8) stated that Heinen's ratio must be used with caution.

In his studies, Brader (2) selected the  $8.57 \mu/10.27\mu$  absorbance ratio in measuring polypropylene crystallinities. This ratio was based on accepting the  $10.27\mu$  band as a true measure of the density-thickness product and the  $8.57\mu$  band as an intrinsic measure of the isotacticity of the base resin.

From their work involving the melting behavior of polypropylene, Abe and Yanagizawa (1) stated that the  $1000 \text{ cm}^{-1}/976 \text{ cm}^{-1}$  absorbance ratio could be used as a relative measure of polypropylene crystallinity. However, Liang and Pearson (7) have stated that this ratio is not a measure of the polypropylene crystallinity. From this same study by Abe and Yanagisawa, it was suggested that the  $1170 \text{ cm}^{-1}/1153 \text{ cm}^{-1}$  absorbance ratio could be a possible measure of polypropylene crystallinities.

Schnell (17) suggested that the relationship between the absorbances of the  $841 \text{ cm}^{-1}$  and the  $998 \text{ cm}^{-1}$  infrared bands is a measure of the crystallinity of polypropylene.

Fraser (4) suggested the use of the relationship,

$$\% \text{ crystallinity} = 109 \frac{A(10.03\mu) - A(10.90\mu)}{A(10.29\mu) - A(10.90\mu)} - 31.4$$

where  $A(10.03\mu)$  is the absorbance of the crystalline sensitive band,  $A(10.29\mu)$  is the absorbance of the internal standard,  $A(10.90\mu)$  is the absorbance of the background, and 109 and

31.4 are factors which give the crystallinity as a per cent, as a good method for obtaining crystallinities for polypropylene from infrared data.

The most thorough infrared approach to polypropylene crystallinity measurements seemed to be that of Quynn et al. (16). The internal standard band chosen was at 10.29 $\mu$ , and the crystalline sensitive bands chosen were at 10.03 $\mu$ , 11.90 $\mu$ , and 12.37 $\mu$ . Background regions were selected for the four bands and the absorbance ratios were established. The absorbance ratio used for the 10.03 $\mu$  and 11.90 $\mu$  crystalline sensitive bands was

$$\frac{A(\lambda) - A(10.90\mu)}{A(10.29\mu) - A(10.90\mu)}$$

and the ratio for the 12.37 $\mu$  band was

$$\frac{A(12.37\mu) - A(12.20\mu)}{A(10.29\mu) - A(10.90\mu)}$$

Each of the ratios was said to reflect the polypropylene's crystallinity.

## CHAPTER III

### EXPERIMENTAL PROCEDURE

#### I. BULK POLYPROPYLENE SAMPLES

Polymers of stereoregular polypropylene, Escon-113 and Escon-125 polymer grades supplied by the Enjay Chemical Company, Pro-fax 6501 grade of polymer supplied by the Hercules Powder Company, and high and low density fractions obtained by the Soxhlet extraction of the three polymer grades with commercial grades of acetone, diethyl ether, and n-heptane, were used in the preparation of the films for this study. The physical properties for the three polypropylene grades are listed in Table I.

#### II. PREPARATION OF POLYPROPYLENE FILMS

Films having different densities and thicknesses were prepared from the bulk polypropylene by hot pressing in a model 20-1301,2, Buehler metallurgical press and heater using various conditions of temperature, pressure, and time. Other films were prepared under various melting, drawing, and quenching conditions on heated glass plates. In addition, films were prepared by casting hot xylene and heptane solutions of the bulk polypropylene on glass plates followed by the evaporation of the solvent.

TABLE I  
 PROPERTIES OF THE BULK POLYPROPYLENE SAMPLES  
 Given by Manufacturer

Property	Escon-113	Escon-125	Pro-fax 6501
Melting point	168°C	168°C	172°C
Softening point	138°C	152°C	---
Intrinsic viscosity	---	---	2.95
Flow rate	low	high	---
Coefficient of linear thermal expansion	6.46x10 in/in/°C	6.46x10 in/in/°C	---
Specific heat at 73° F	0.46 cal/g	0.46 cal/g	---
Density at 73° F	0.902 g/cc	0.902 g/cc	---
Weight average molecular weight	---	---	659,000 (Wesslau)
Number average molecular weight	---	---	55,000 (Wesslau)
Burning rate	slow	slow	---
Water absorption	0.01%	0.01%	---
Chemical resistance to acids	good	good	---
Chemical resistance to alkalis	excellent	excellent	---
Chemical resistance to organic solvents	good	good	---

The specific conditions employed in the preparations of the various films were presented in Tables II, III, and IV.

### III. DENSITY DETERMINATIONS OF THE BULK POLYPROPYLENE AND THE PREPARED FILMS

The densities, at  $28 \pm 0.2^\circ\text{C}$ , of the original polypropylene and the prepared films were measured by flotation and density gradient methods carried out in a thermoregulated constant temperature water bath.

#### Densities by the Flotation Method

The flotation method was performed by first establishing a calibration curve of refractive index, measured with a model 37754, Zeiss Abbe refractometer, and density, measured by means of a pycnometer, at the specified temperature, for the density medium of toluene and carbon tetrachloride. The data and resulting refractive index-density calibration curve are given in Table V and Figure 2, respectively.

The measurement of polypropylene densities by flotation consisted first of inserting a small piece of the bulk polymer or film into a test tube, containing carbon tetrachloride, which was almost totally immersed in the constant temperature water bath. Toluene was then



TABLE II

CONDITIONS FOR THE PREPARATION OF FILMS FROM THE BULK POLYPROPYLENE  
SAMPLES USING THE BUEHLER METALLURGICAL PRESS AND HEATER

Sample	Polymer grade	Pressing conditions	Cooling conditions
E-100	Escon-113	182°C at 2000 psi. for 10 min. 182°C at 8000 psi. for 10 min.	28°C (for air cooled Al cooling block) at 8000 psi. for 1 hr.
E-101	Escon-113	182°C at 2000 psi. for 15 min. 182°C at 6000 psi. for 5 min.	26.5°C (for air cooled Al cooling block) at 6000 psi. for 2 hr.
E-102	Escon-113	182°C at 0 psi. for 17 min. 182°C at 8000 psi. for 3 min.	27°C (for air cooled Al cooling block) at 8000 psi. for 30 min.
E-103	Escon-113	182°C at 0 psi. for 10 min. 182°C at 8000 psi. for 10 min.	21°C (for water cooled Al cooling block) at 8000 psi. for 30 min.
E-104	Escon-113	175°C at 0 psi. for 20 min. 175°C at 8000 psi. for 20 min.	23°C (for water cooled Al cooling block) at 8000 psi. for 30 min.
E-105	Escon-113	182°C at 4000 psi. for 10 min. 182°C at 8000 psi. for 15 min.	28°C (for insulated Al cooling block) at 8000 psi. for 1 hr.
E-106	Escon-113	182°C at preload for 15 min. 182°C at 8000 psi. for 5 min.	28.5°C (for air cooled Al cooling block) at 8000 psi. for 1 hr.
E-107	Escon-113	182°C at 2000 psi. for 10 min. 182°C at 7000 psi. for 10 min.	<-50°C (for dry ice-acetone cooled Al cooling block) at 7000 psi. for 15 min.
E-108	Escon-113	182°C at 2000 psi. for 20 min. 182°C at 8000 psi. for 5 min.	<-50°C (for dry ice-acetone cooled Al cooling block) at 8000 psi. for 15 min.

TABLE II (continued)

Sample	Polymer grade	Pressing conditions	Cooling conditions
E-109	Escon-113 heptane residue	182°C at 0 psi. for 15 min. 182°C at 6000 psi. for 6 min.	26°C (for air cooled Al cooling block) at 6000 psi. for 30 min.
E-110	Escon-113	182°C at 2000 psi. for 10 min. 182°C at 7000 psi. for 10 min.	5°C (for ice-water cooled Al cooling block) at 7000 psi. for 30 min.
E-111	Escon-113	182°C at 0 psi. for 10 min. 182°C at 8000 psi. for 5 min.	21°C (for water cooled Al cooling block) at 8000 psi. for 1 hr.
E-112	Escon-113	182°C at 2000 psi. for 15 min. 182°C at 8000 psi. for 5 min.	26°C (for air cooled Al cooling block) at 8000 psi. for 1 hr.
E-200	Escon-125	182°C at 0 psi. for 10 min. 182°C at 8000 psi. for 10 min.	27.5°C (for air cooled Al cooling block) at 8000 psi. for 1 hr.
E-201	Escon-125	182°C at 2000 psi. for 10 min. 182°C at 8000 psi. for 10 min.	8°C (for ice-water cooled Al cooling block) at 8000 psi. for 1 hr.
E-202	Escon-125	182°C at preload for 5 min. 182°C at 9500 psi. for 15 min.	25.5°C (for air cooled Al cooling block) at 9500 psi. for 1 hr.
E-203	Escon-125 heptane residue	182°C at 2000 psi. for 10 min. 182°C at 8000 psi. for 10 min.	26°C (for insulated Al cooling block) at 8000 psi. for 1 hr.
P-100	Pro-fax 6501 acetone, ether heptane residue	182°C at 2000 psi. for 15 min. 182°C at 6000 psi. for 5 min.	28°C (for insulated Al cooling block) at 6000 psi. for 1 hr.

TABLE II (continued)

Sample	Polymer grade	Pressing conditions	Cooling conditions
F-101	Pro-fax 6501 heptane residue	182°C at 6000 psi. for 5 min. 182°C at 6000 psi. for 5 min.	27°C (for insulated Al cooling block) at 6000 psi. for 1 hr.
P-102	Pro-fax 6501	182°C at 0 psi. for 12 min. 182°C at 8000 psi. for 10 min.	26.5°C (for insulated Al cooling block) at 8000 psi. for 1 hr.
P-103	Pro-fax 6501 heptane residue	182°C at 0 psi. for 20 min. 182°C at 8000 psi. for 10 min.	27°C (for insulated Al cooling block) at 8000 psi. for 2 hr.

TABLE III  
 CONDITIONS FOR THE PREPARATION OF FILMS FROM THE BULK POLYPROPYLENE  
 SAMPLES BY MELTING AND DRAWING ON HOT GLASS PLATES

Sample	Polymer grade	Melting conditions	Drawing conditions	Cooling conditions
E-300	Escon-113	175°C (on hot plate) for 10 min.	178°C (with glass plate) for 1 min.	<-50°C in acetone-dry ice for 15 min.
E-301	Escon-113	175°C (on hot plate) for 12 min.	180°C (with glass plate) for 1 min.	28°C in air for 1 hr.
E-400	Escon-125	179°C (on hot plate) for 10 min.	180°C (with glass plate) for 1 min.	<-50°C in acetone-dry ice for 15 min.
P-200	Pro-fax 6501	180°C (on hot plate) for 7 min.	184°C (with glass plate) for 1 min.	20°C in water for 5 min.

TABLE IV

CONDITIONS FOR THE PREPARATION OF FILMS FROM THE BULK POLYPROPYLENE  
 SAMPLES BY SOLVENT DISSOLUTION AND EVAPORATION

Sample	Polymer grade	Dissolving conditions	Evaporating conditions method temperature time between layers	Cooling conditions
E-500	Escon-113	4.5 g/250 ml xylene at 180°C	hot plate 140°C 20 sec.	water at 22°C for 10 min.
E-501	Escon-113 heptane soluble	0.5 g/50 ml xylene at 170°C	hot plate 140°C 25 sec.	air at 26°C for 30 min.
E-600	Escon-125	5 g/250 ml xylene at 180°C	hot plate 140°C 30 sec.	ice-water at 4°C for 15 min.
E-601	Escon-125 heptane soluble	1.55 g/125 ml heptane at 140°C	oven 100°C ----	air at 25°C for 30 min.
E-602	Escon-125 heptane soluble	1.2 g/100 ml heptane at 135°C	oven 105°C ----	water at 21°C for 10 min.
P-300	Pro-fax 6501	5 g/250 ml xylene at 180°C	hot plate 140°C 30 sec.	water at 24°C for 5 min.
P-301	Pro-fax 6501	4.75 g/250 ml xylene at 170°C	hot plate 140°C 25 sec.	water at 23.5°C for 10 min.

TABLE V  
 DENSITIES AND REFRACTIVE INDICES FOUND BY USING  
 A PYCNOMETER FOR TOLUENE AND CARBON  
 TETRACHLORIDE SOLUTIONS

Sample	Temperature	Refractive index	Density
Toluene	27.8°C	1.4935	0.874 g/ml
Toluene-CCl <sub>4</sub> mixture 1	28.0°C	1.4922	0.913 g/ml
Toluene-CCl <sub>4</sub> mixture 2	27.8°C	1.4910	0.930 g/ml
Toluene-CCl <sub>4</sub> mixture 3	27.9°C	1.4835	1.125 g/ml
Toluene-CCl <sub>4</sub> mixture 4	27.9°C	1.4995	0.992 g/ml
Toluene-CCl <sub>4</sub> mixture 5	28.1°C	1.4875	1.050 g/ml
Toluene-CCl <sub>4</sub> mixture 6	28.0°C	1.4810	1.157 g/ml
Toluene-CCl <sub>4</sub> mixture 7	28.2°C	1.4765	1.256 g/ml
Toluene-CCl <sub>4</sub> mixture 8	27.9°C	1.4709	1.348 g/ml
Toluene-CCl <sub>4</sub> mixture 9	28.2°C	1.4572	1.602 g/ml

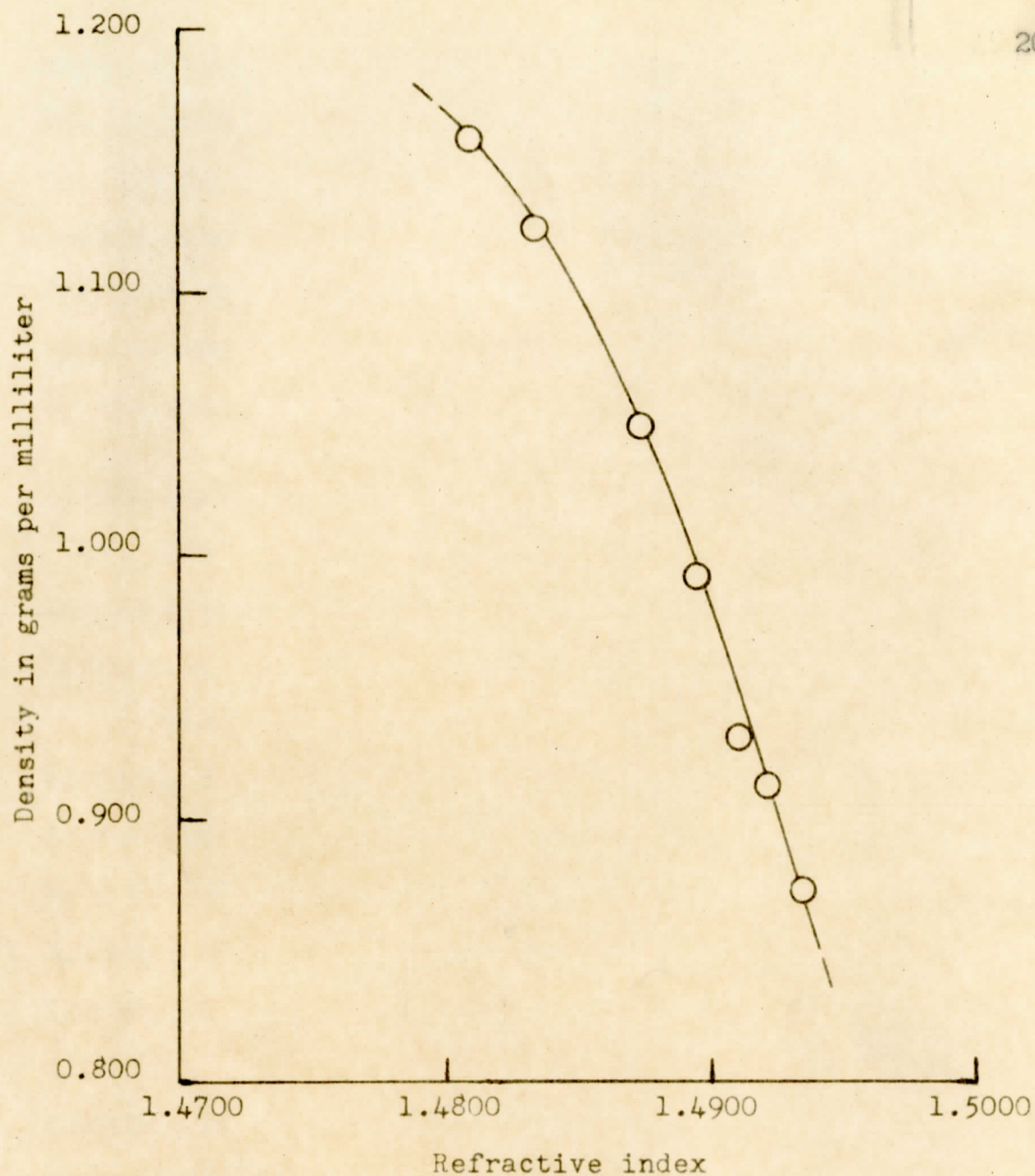


FIGURE 2

RELATIONSHIP BETWEEN THE DENSITIES AND THE REFRACTIVE INDICES OF TOLUENE AND CARBON TETRACHLORIDE SOLUTIONS AT  $28 \pm .2^{\circ}$  CENTIGRADE

added stepwise to the test tube, with constant stirring, until the polypropylene sample assumed a position in the center of the liquid and showed no tendency to change its position for thirty minutes. The density of the liquid was taken to be the same as that for the polymer sample. The liquid densities were determined by measuring its refractive index followed by the use of the pre-established calibration curve.

#### Densities by the Density Gradient Method

The density gradient method of density determination involved the construction of a density gradient tube, calibration of the tube, and the actual density measurements.

The gradient tube assembly is shown in Figure 3. Two beakers, A and B, containing high and low density toluene-carbon tetrachloride mixtures, respectively, were connected by a "T" with a glass bulb. From A, constantly stirred, a delivery tube with a two-way stopcock carried the mixed liquid, by siphoning action, to the inner edge of a graduated cylinder. The cylinder, nearly immersed in a constant temperature water bath, was slowly filled so as to give continuously decreasing density layers from the bottom to the top of the cylinder.

The gradient tube was calibrated by means of glass bulbs of predetermined density which sought the graduated cylinder levels corresponding to their density. The bulb densities and corresponding cylinder levels are recorded



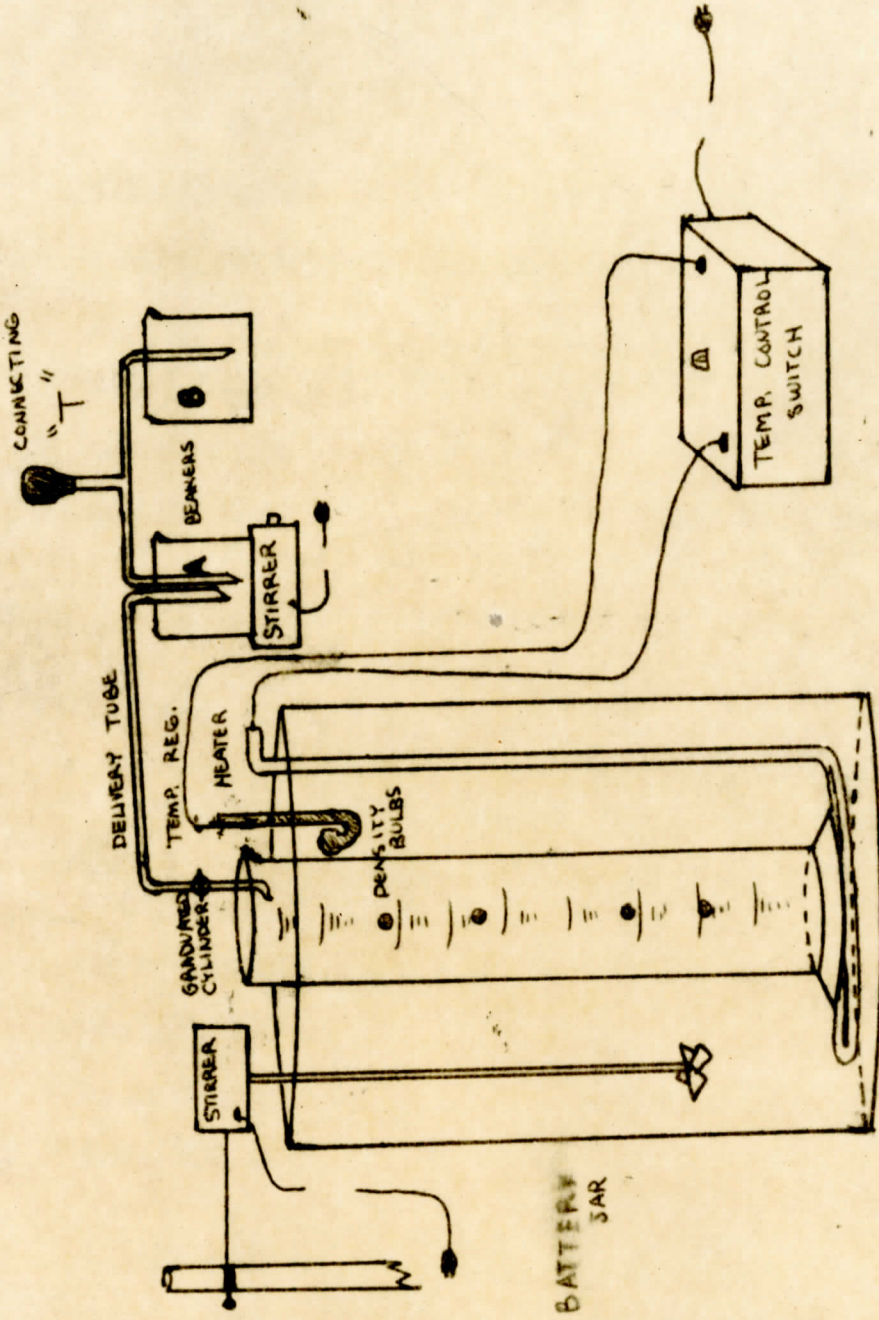


FIGURE 3  
ASSEMBLY FOR DENSITY GRADIENT MEASUREMENTS

in Table VI, and the calibration curve produced by this data is plotted in Figure 4. The plot shows that a linear gradient exists.

To measure the polypropylene film densities, a small film fragment was inserted just under the surface of the liquid in the gradient tube, and it was allowed to fall slowly to a level corresponding to its density. This required a short time, usually less than fifteen minutes. After thirty minutes the level of the film in the gradient tube was noted, and the density was obtained from the calibration curve.

#### IV. INFRARED STUDIES OF POLYPROPYLENE FILMS

##### Typical Stereoregular Polypropylene

A film of polypropylene, prepared from hot-pressed Escon-113, was inserted into the sample compartment of the model IR-7, Beckman infrared spectrophotometer. Using double beam operation and appropriate conditions of slit program, period, gain, and scanning speed which gave bands with a high degree of resolution, an infrared absorption spectrum from  $600\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  was obtained for the film sample.

##### Polypropylene Samples Varying in Density or Thickness

The procedure described for obtaining the spectrum of a typical stereoregular polypropylene was used to obtain the infrared spectra for the prepared films which varied in density and thickness. The same procedure was, also, used

TABLE VI

CORRELATION BETWEEN THE POSITIONS OF THE GLASS DENSITY  
BULBS IN THE CYLINDER AND THEIR DENSITIES

Bulb number	Bulb density	Bulb position
1	0.917 g/ml	275 ml
2	0.923 g/ml	199 ml
3	0.931 g/ml	99 ml
4	0.934 g/ml	55 ml

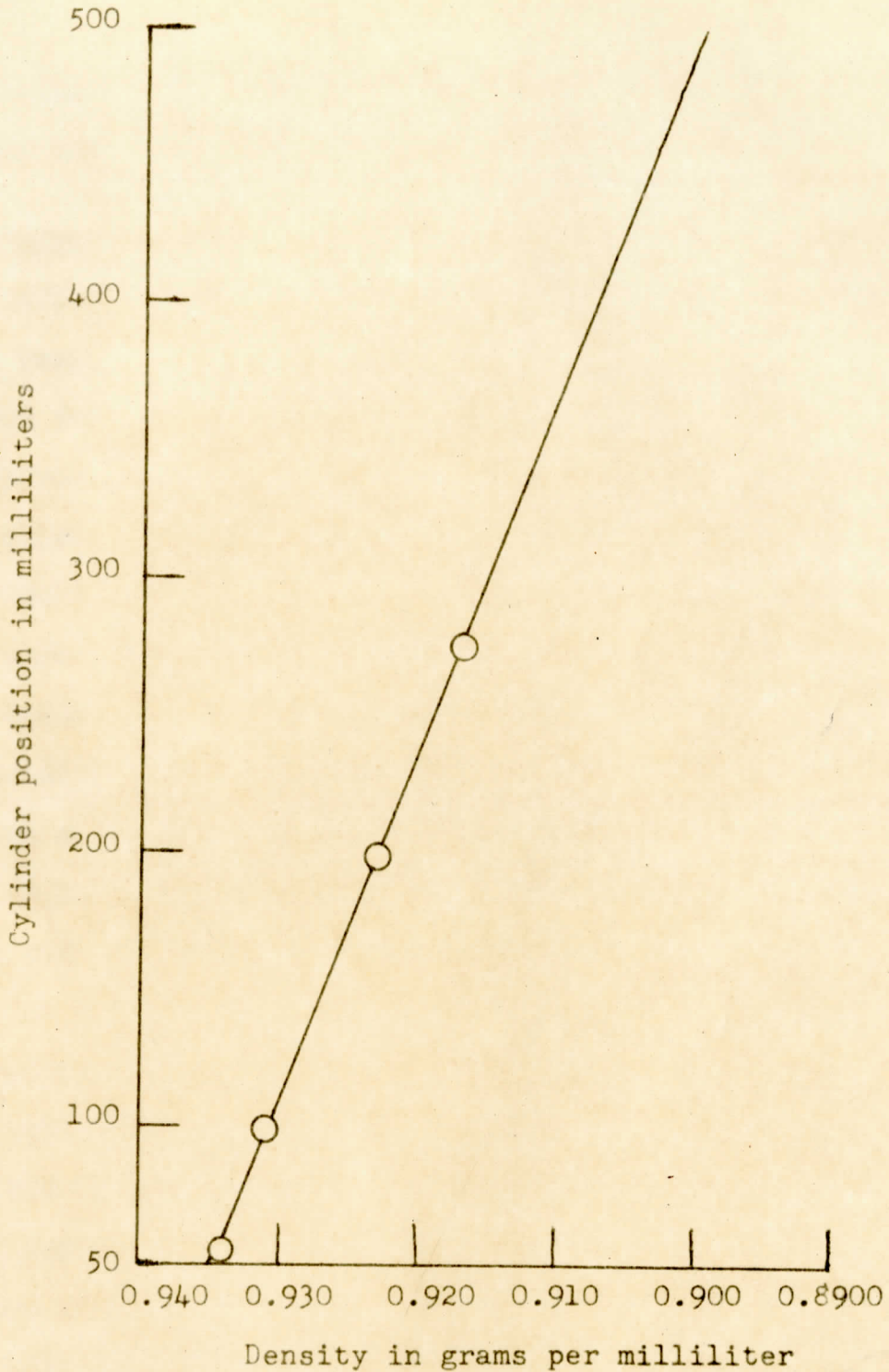


FIGURE 4

RELATIONSHIP BETWEEN DENSITY AND CYLINDER  
POSITION FOR THE DENSITY GRADIENT TUBE

in obtaining the infrared spectra for a film series of polypropylene having the same density but different thicknesses.

#### Heated Polypropylene Sample

Infrared spectra for a hot-pressed Escon-113 film at various temperatures were obtained using the method as described for the typical stereoregular film except with a Perkin-Elmer, model S-105/29E heated cell having polished sodium chloride windows and with a thermocouple and temperature measuring assembly in association with the IR-7 spectrophotometer.

Before using the cell, the thermocouple's arbitrary meter readings were calibrated in degrees Centigrade with glycerine maintained at different constant temperatures. Table VII and Figure 5 give the data obtained in the calibration and the resulting calibration curve.

The thick and unpolished sodium chloride windows had to be reduced in thickness and polished before use with the heated cell. Grinding of the windows was performed with a medium and then a fine grade of sandpaper to give a thickness of approximately 25.1 mm. The surfaces of the windows were then rough polished by a rotary motion of the windows on slightly moistened levigated alumina powder placed on a flannel cloth and then on dry alumina on the cloth. The fine polishing was done by first slightly dampening a clean flannel cloth and quickly rubbing the surface of the window

TABLE VII

RELATIONSHIP BETWEEN THE METER READINGS OF THE PERKIN-ELMER  
HEATED CELL AND THE CENTIGRADE TEMPERATURE

Observation	Centigrade temperature	Meter reading
1	50 °	8.2
2	75 °	17.2
3	100 °	26.2
4	110 °	30.0
5	120 °	33.5
6	130 °	37.0
7	140 °	40.6
8	150 °	44.4
9	160 °	48.0
10	170 °	51.5
11	180 °	55.2
12	190 °	58.6

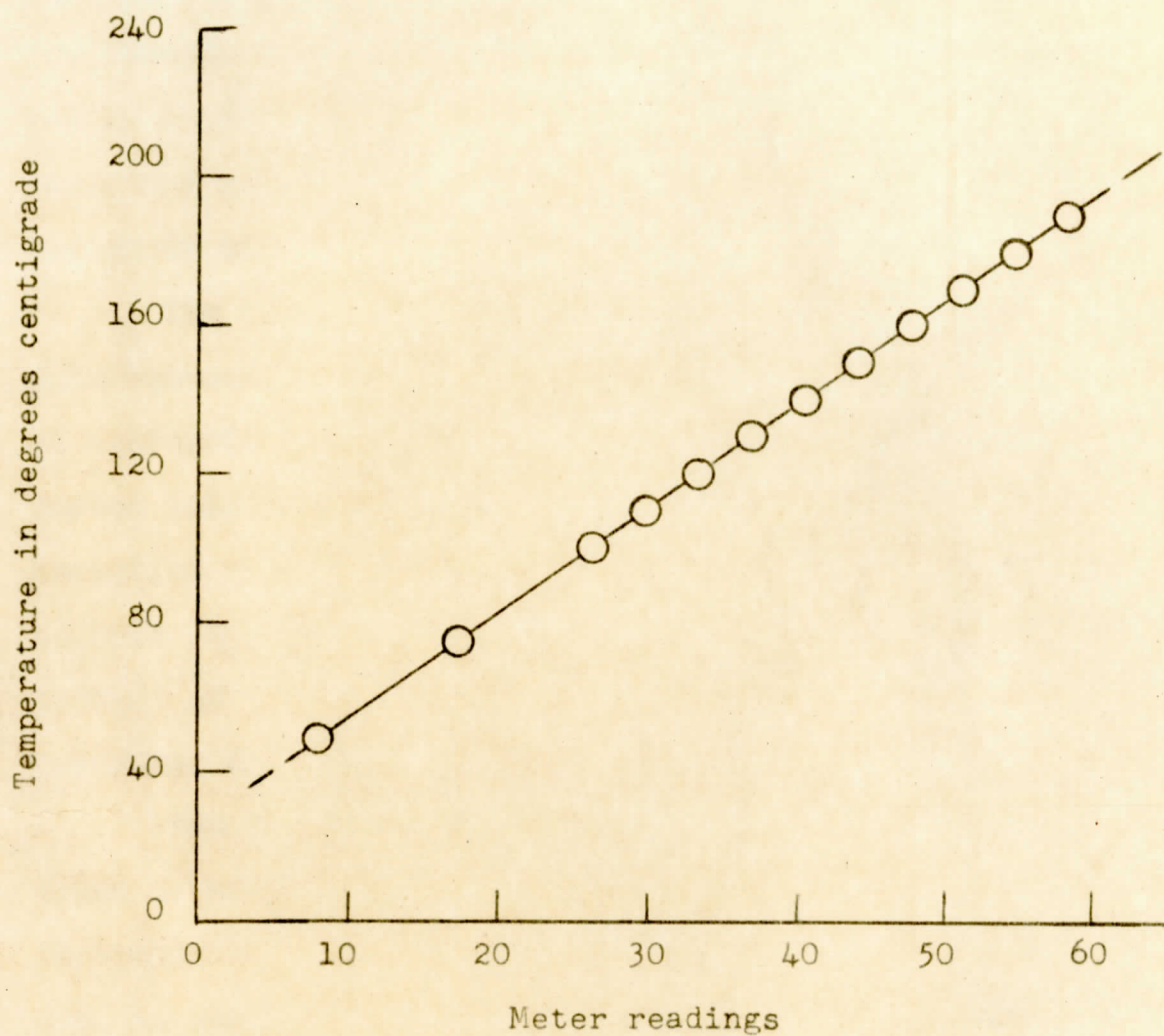


FIGURE 5

THE RELATIONSHIP BETWEEN THE METER READINGS  
OF THE PERKIN-ELMER HEATED CELL AND  
THE CENTIGRADE TEMPERATURE

with it and this was followed immediately by rubbing with a dry flannel cloth. Finally, the surface was rubbed alternately on dry flannel cloth and chamois. The polishing procedure gave sodium chloride windows which were smooth and quite transparent.

The heated cell was prepared by sandwiching the polymer film between the polished windows separated by a lead spacer of appropriate thickness. Next, the sandwiched film was inserted into the heated cell assembly, and the entire assembled unit was placed into the sample compartment of the Beckman IR-7 spectrophotometer. The infrared absorption spectra of the film were obtained at various constant temperatures ranging from 30°C to, and including, 190°C.

The infrared spectra were studied with respect to the bands affected by the temperature treatment in terms of sharpness and intensity and the appearance of new bands, if any, in the spectra. An absorbance ratio for four of the crystalline sensitive bands was calculated from the spectra obtained at various temperatures. The absorbance ratio,  $\chi$ , was defined by

$$\chi = \frac{A_{\gamma c} - B_{\gamma a}}{A_{\gamma s} - B_{\gamma b}};$$

where  $A_{\gamma c}$  was the crystalline dependent band absorbance, examples being the 822 cm<sup>-1</sup>, 843 cm<sup>-1</sup>, 902 cm<sup>-1</sup>, and 1002 cm<sup>-1</sup> bands;  $B_{\gamma a}$  was the background absorbance for the particular crystalline band used, 827 cm<sup>-1</sup> for the 812 cm<sup>-1</sup> band and



925  $\text{cm}^{-1}$  for the other three bands;  $A\gamma_s$  was the absorbance of the band used as an internal standard band, 1170  $\text{cm}^{-1}$  in this instance; and  $B\gamma_b$  was the background absorbance for the internal standard band, 1205  $\text{cm}^{-1}$  in this case. This ratio was determined previously for films of comparable density but different thicknesses and found to be an effective method for nearly eliminating a thickness variable from the experimental work, thus, it was selected for use in this segment of the work as it also was for the films ranging in density.

From the data collected in the experimental procedure, temperature-absorbance, thickness-absorbance, and specific volume-absorbance relationships were determined for certain crystalline sensitive infrared absorption bands.

## CHAPTER IV

### RESULTS AND DISCUSSION OF RESULTS

#### I. POLYPROPYLENE DENSITIES

##### Original Samples

The densities of the three original polypropylene bulk samples, Escon-113, Escon-125, and Pro-fax 6501, are given in Table VIII. The Pro-fax 6501 exhibits the highest average density value at 0.930 g/ml and the Escon-125 the lowest value at 0.909 g/ml. The Escon-113 and Pro-fax 6501 densities are similar in that their values are fairly uniform and slightly more uniform than the Escon-125 densities.

##### Prepared Films

Table IX lists the measured densities, calculated specific volumes, found by taking the reciprocal of the densities, and the calculated crystallinities, found using the relationship

$$\% \text{ crystallinity} = \frac{\rho_x - \rho_a}{\rho_c - \rho_a} \cdot \frac{\rho_c}{\rho_x} \times 100$$

where  $\rho_x$  is the density measured for a sample x,  $\rho_c$  and  $\rho_a$  are Natta's (12) density values for completely crystalline and completely amorphous polypropylene, respectively, for the polypropylene films prepared under a variety of conditions. Although no completely amorphous samples are included, the

TABLE VIII

DENSITIES DETERMINED FOR THE ORIGINAL ESCON-113,  
 ESCON-125, AND PRO-FAX 6501 POLYPROPYLENES

Sample	Density		
	Escon-113	Escon-125	Pro-fax 6501
1	0.916 g/ml	0.906 g/ml	0.927 g/ml
2	0.912 g/ml	0.910 g/ml	0.931 g/ml
3	0.916 g/ml	0.931 g/ml	0.935 g/ml
4	0.926 g/ml	0.902 g/ml	0.936 g/ml
5	0.922 g/ml	0.910 g/ml	0.923 g/ml
6	0.916 g/ml	0.900 g/ml	0.931 g/ml
7	0.924 g/ml	0.906 g/ml	0.934 g/ml
8	0.922 g/ml	0.900 g/ml	0.938 g/ml
9	0.912 g/ml	0.914 g/ml	0.934 g/ml
10	0.913 g/ml	0.914 g/ml	0.931 g/ml
Average	0.918 g/ml	0.909 g/ml	0.930 g/ml

TABLE IX

DENSITIES, CALCULATED SPECIFIC VOLUMES AND CALCULATED  
CRYSTALLINITIES FOR THE POLYPROPYLENE FILMS  
USED IN THIS STUDY

Sample	Density	Specific volume	Percent crystallinity
E-100	0.921 g/ml	1.086 ml/g	84
E-101	0.924 g/ml	1.082 ml/g	87
E-102	0.922 g/ml	1.084 ml/g	85
E-103	0.913 g/ml	1.095 ml/g	75
E-104	0.916 g/ml	1.092 ml/g	79
E-105	0.921 g/ml	1.086 ml/g	84
E-106	0.921 g/ml	1.086 ml/g	84
E-107	0.901 g/ml	1.110 ml/g	62
E-108	0.901 g/ml	1.110 ml/g	62
E-109	0.926 g/ml	1.080 ml/g	90
E-110	0.917 g/ml	1.090 ml/g	80
E-111	0.926 g/ml	1.080 ml/g	90
E-112	0.924 g/ml	1.082 ml/g	87
E-200	0.915 g/ml	1.092 ml/g	77
E-201	0.920 g/ml	1.087 ml/g	83
E-202	0.915 g/ml	1.092 ml/g	77
E-203	0.926 g/ml	1.080 ml/g	90
P-100	0.922 g/ml	1.084 ml/g	85
P-101	0.934 g/ml	1.071 ml/g	98
P-102	0.934 g/ml	1.071 ml/g	98
P-103	0.933 g/ml	1.072 ml/g	97
E-300	0.908 g/ml	1.101 ml/g	70
E-301	0.913 g/ml	1.095 ml/g	75
E-400	0.901 g/ml	1.110 ml/g	62
P-200	0.912 g/ml	1.096 ml/g	74
E-500	0.932 g/ml	1.073 ml/g	96
E-501	0.888 g/ml	1.126 ml/g	46
E-500	0.902 g/ml	1.108 ml/g	63
E-601	0.870 g/ml	1.149 ml/g	25
E-602	0.866 g/ml	1.155 ml/g	20
P-300	0.933 g/ml	1.072 ml/g	97
P-301	0.935 g/ml	1.069 ml/g	99

densities range from 0.866 g/ml to 0.935 g/ml. This density range would indicate that films from the sample bulk polypropylene can be produced through the use of various extraction, dissolution, heating, pressing, and quenching conditions, which vary greatly in crystallinity.

## II. POLYPROPYLENE INFRARED STUDIES

### Typical Stereoregular Polypropylene

Figure 6 shows the infrared spectrum for an Escon-113 pressed film having a density of 0.920 g/ml and a thickness of 0.09 mm. The wavenumbers for the absorption bands found in the spectrum together with their relative sharpnesses and intensities (absorbances) are shown in Table X. The infrared absorption bands found in the spectrum are nearly identical with those found by other investigators (1)(8)(9)(19).

### Thickness Effects

In Table XI the absorbance ratios of the 812  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ , 902  $\text{cm}^{-1}$ , and 1002  $\text{cm}^{-1}$  bands to the 1170  $\text{cm}^{-1}$  band, after background absorbances have been subtracted, for the spectra of films having the same density but different thicknesses are listed. Inspection of this information shows that the intensity ratio, as established, did not change significantly with changes in film thickness. It appears, therefore, that an intensity correction for thickness differences

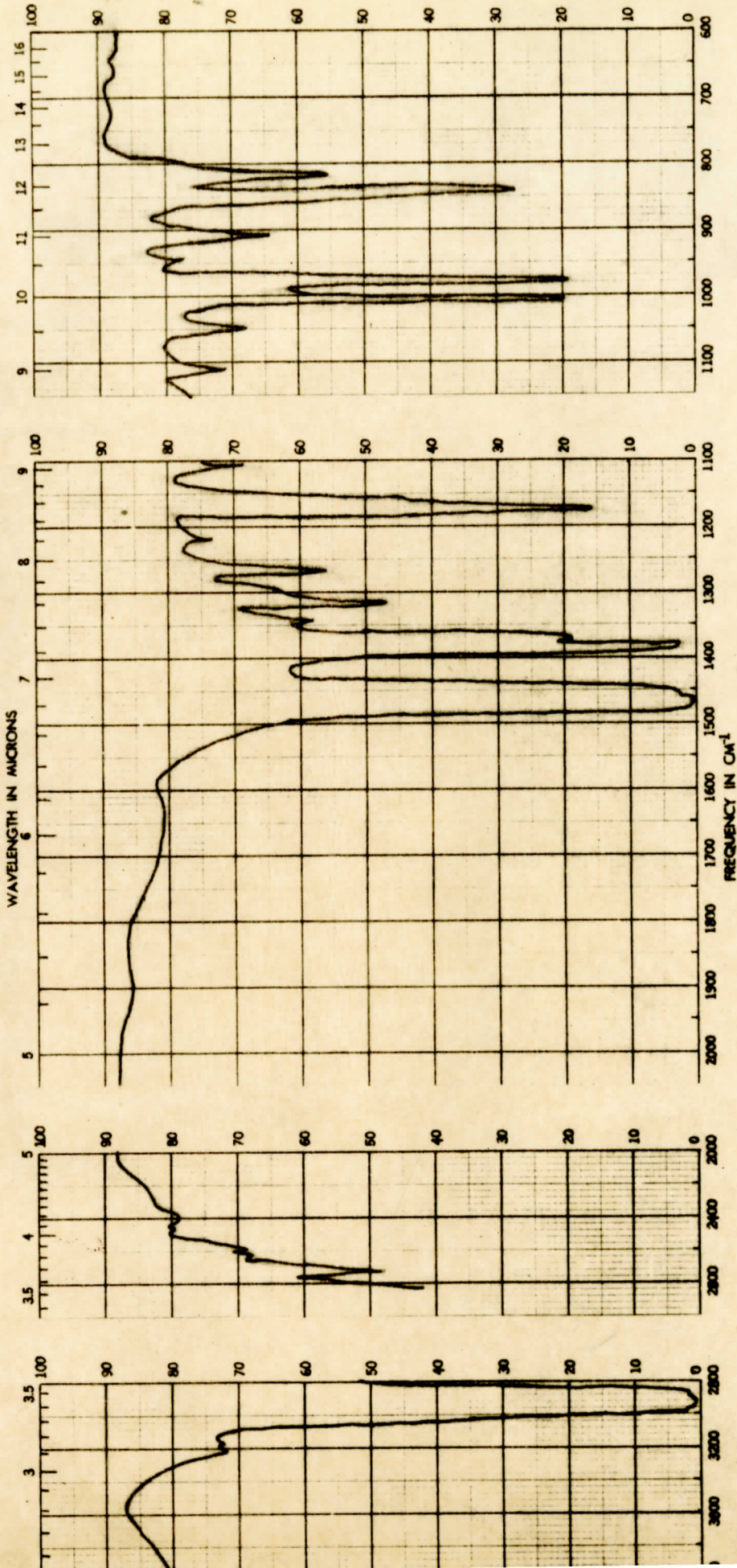


FIGURE 6

INFRARED SPECTRUM OF A TYPICAL CRYSTALLINE POLYPROPYLENE  
FILM USING THE BECKMAN IR-7 SPECTROPHOTOMETER

TABLE X

INDEXING OF THE BANDS PRESENT IN THE INFRARED  
SPECTRUM OF POLYPROPYLENE FROM FIGURE 6

Band wave number	Absorbance	Description
812 cm	0.26	sharp
843 cm	0.55	sharp, deep
902 cm	0.22	sharp
943 cm	0.82	doublet of same intensity
976 cm	0.92	sharp, deep
1002 cm	0.71	sharp, deep
1048 cm	0.16	sharp
1107 cm	0.16	relatively sharp
1159 cm	0.35	shoulder band
1170 cm	0.83	sharp, deep, moderately broad
1223 cm	0.14	relatively sharp
1262 cm	0.26	sharp
1302 cm	0.21	weak, shoulder band
1308 cm	0.34	sharp
1332 cm	0.24	relatively sharp
1364 cm	0.74	relatively sharp, shoulder band
1380 cm	1.85	relatively sharp, deep
1462 cm	∞	deep, very broad
1478 cm	1.26	deep, very weak, shoulder band
2598 cm	0.17	weak, shoulder band
2638 cm	0.17	weak, shoulder band
2740 cm	0.32	sharp, shoulder band
2850 cm	0.32	sharp, shoulder band
2980 cm	∞	wide, deep
3160 cm	0.15	weak, shoulder band
3210 cm	0.15	weak, shoulder band

TABLE XI

THICKNESS AND ABSORBANCE RATIO RELATIONSHIPS FOR THE  
812  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ , 902  $\text{cm}^{-1}$ , AND 1002  $\text{cm}^{-1}$   
INFRARED BANDS OF POLYPROPYLENE

Sample	Thickness	Infrared band	Absorbance ratio	Deviation
T-1	0.112 mm	812 $\text{cm}^{-1}$	0.25	0.01
T-2	0.205 mm	812 $\text{cm}^{-1}$	0.27	0.03
T-3	0.057 mm	812 $\text{cm}^{-1}$	0.24	-0.01
T-4	0.071 mm	812 $\text{cm}^{-1}$	0.22	-0.02
T-5	0.038 mm	812 $\text{cm}^{-1}$	0.22	-0.02
T-6	0.080 mm	812 $\text{cm}^{-1}$	0.25	0.01
Average	----	----	0.24	----
T-1	0.112 mm	843 $\text{cm}^{-1}$	0.64	-0.04
T-2	0.205 mm	843 $\text{cm}^{-1}$	0.69	0.01
T-3	0.057 mm	843 $\text{cm}^{-1}$	0.70	0.02
T-4	0.071 mm	843 $\text{cm}^{-1}$	0.67	-0.01
T-5	0.038 mm	843 $\text{cm}^{-1}$	0.71	0.03
T-6	0.080 mm	843 $\text{cm}^{-1}$	0.67	-0.01
Average	----	----	0.68	----
T-1	0.112 mm	902 $\text{cm}^{-1}$	0.22	0.02
T-2	0.205 mm	902 $\text{cm}^{-1}$	0.23	0.03
T-3	0.057 mm	902 $\text{cm}^{-1}$	0.19	-0.01
T-4	0.071 mm	902 $\text{cm}^{-1}$	0.19	-0.01
T-5	0.038 mm	902 $\text{cm}^{-1}$	0.18	-0.02
T-6	0.080 mm	902 $\text{cm}^{-1}$	0.18	-0.02
Average	----	----	0.20	----
T-1	0.112 mm	1002 $\text{cm}^{-1}$	0.81	0.01
T-2	0.205 mm	1002 $\text{cm}^{-1}$	0.80	0.00
T-3	0.057 mm	1002 $\text{cm}^{-1}$	0.81	0.01
T-4	0.071 mm	1002 $\text{cm}^{-1}$	0.79	-0.01
T-5	0.038 mm	1002 $\text{cm}^{-1}$	0.81	0.01
T-6	0.080 mm	1002 $\text{cm}^{-1}$	0.79	-0.01
Average	----	----	0.80	----



can be effected with confidence by using an internal standard absorption band. The  $1170\text{ cm}^{-1}$  infrared band seems to be satisfactory for this internal standard. Other absorbance ratios using various internal standard absorption bands which have been previously reported (2)(6)(16)(17) were tried with fair agreement; however, the  $1170\text{ cm}^{-1}$  infrared band's absorbance minus its background absorbance at  $1205\text{ cm}^{-1}$  when used as the internal standard in conjunction with other absorbance bands minus their backgrounds, seems to give the best agreement from thickness to thickness.

#### Heating Effects

Figures 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, and 19 depict the infrared spectra of an Escon-113 film at temperatures of  $30^\circ$ ,  $50^\circ$ ,  $75^\circ$ ,  $100^\circ$ ,  $110^\circ$ ,  $120^\circ$ ,  $130^\circ$ ,  $140^\circ$ ,  $150^\circ$ ,  $160^\circ$ ,  $170^\circ$ ,  $180^\circ$ , and  $190^\circ\text{C}$ , respectively. The infrared spectra for the film at  $30^\circ$ ,  $50^\circ$ , and  $75^\circ\text{C}$  are nearly identical with respect to the absorption bands' positions and intensities. At  $100^\circ\text{C}$  a more pronounced change occurs in the infrared spectra of the sample with the broadening of certain bands and the decreasing of intensities of certain bands to some degree. This effect increases, somewhat, up to  $120^\circ\text{C}$ . At  $130^\circ\text{C}$ , a more rapid decrease in the absorptions of certain bands occurs in conjunction with continued broadening by most of the bands in the spectra; certain bands begin to lose their

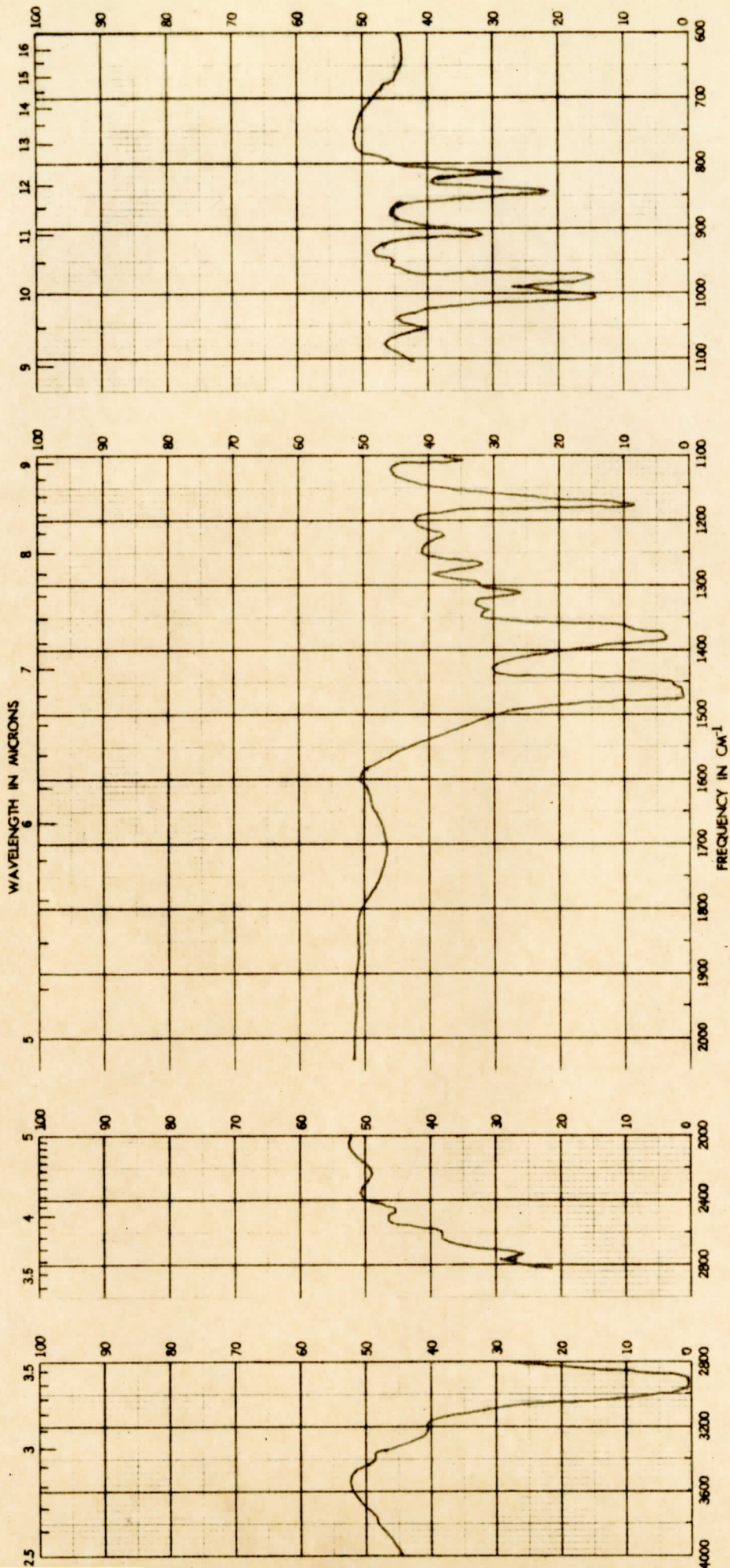


FIGURE 7

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $30 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

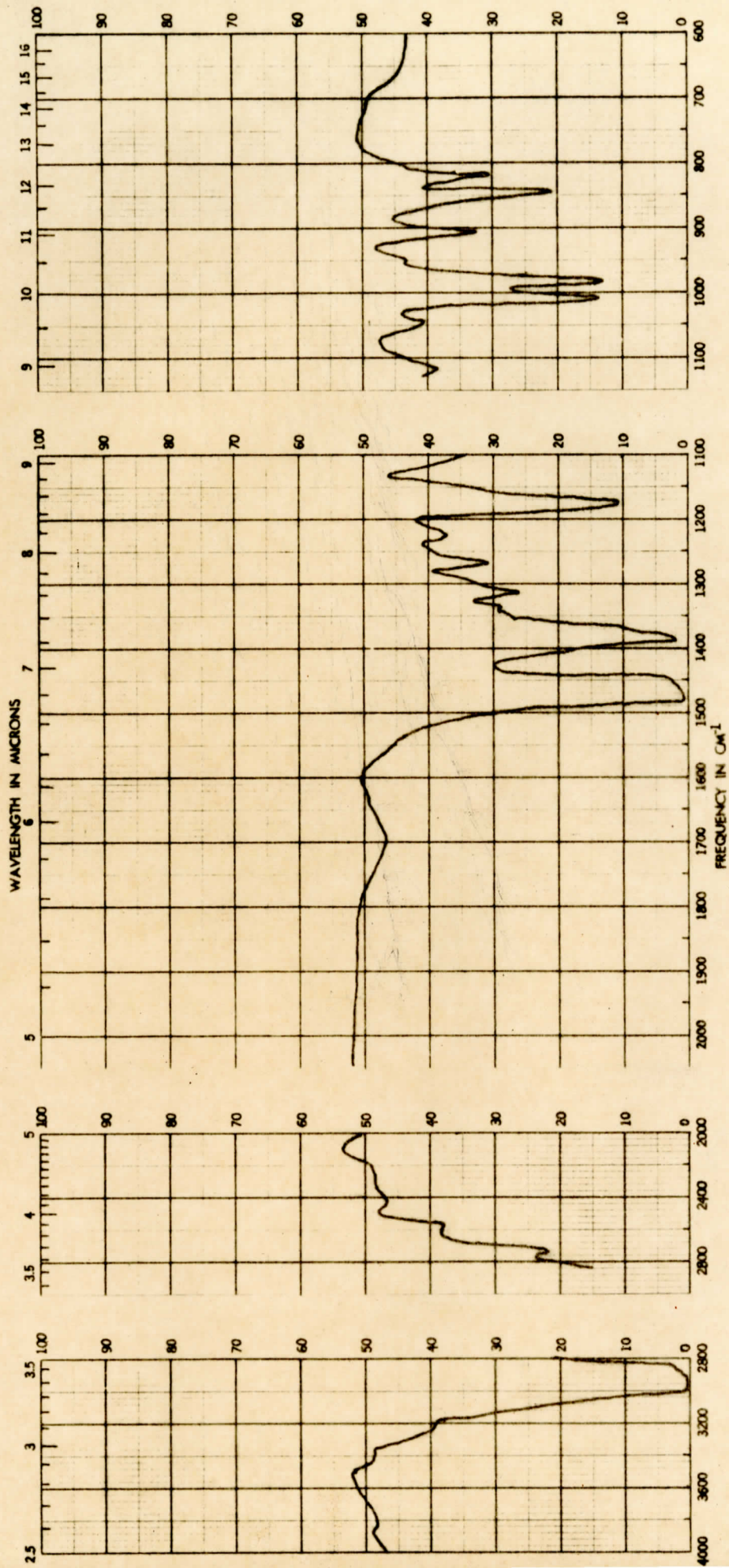


FIGURE 8

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $50 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL  
 AND THE BECKMAN IR-7 SPECTROPHOTOMETER

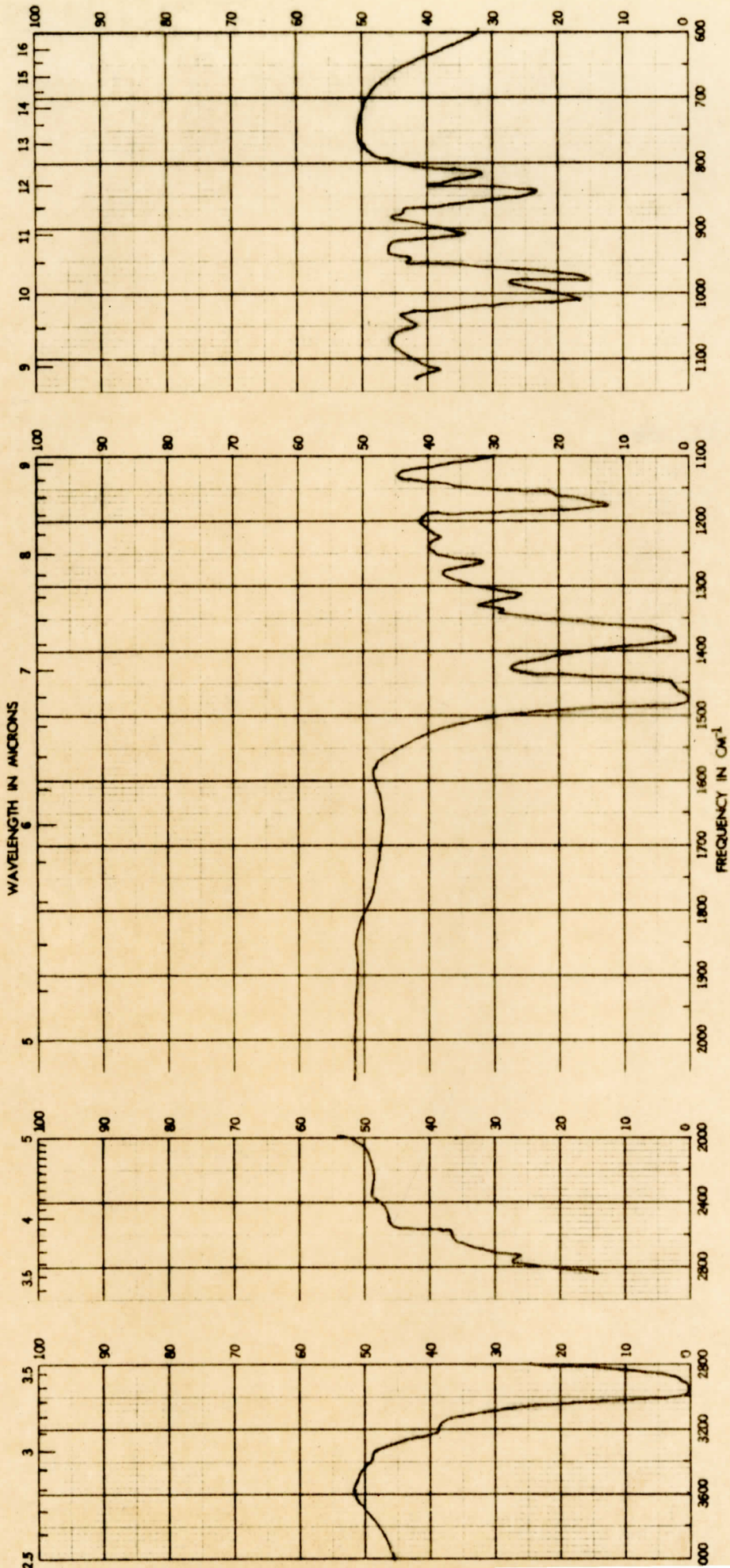


FIGURE 9

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE SAMPLE AT  $75 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

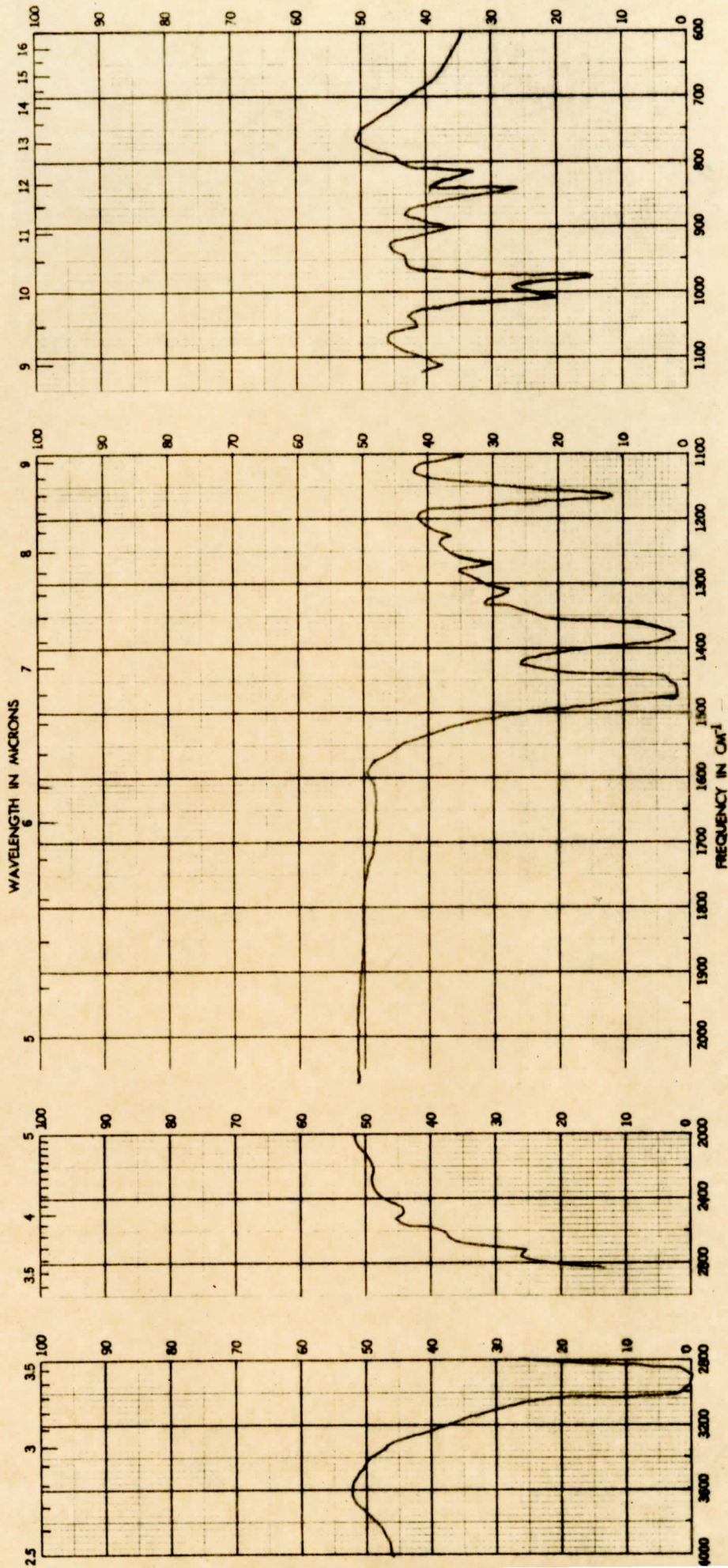


FIGURE 10

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE SAMPLE AT  $100 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

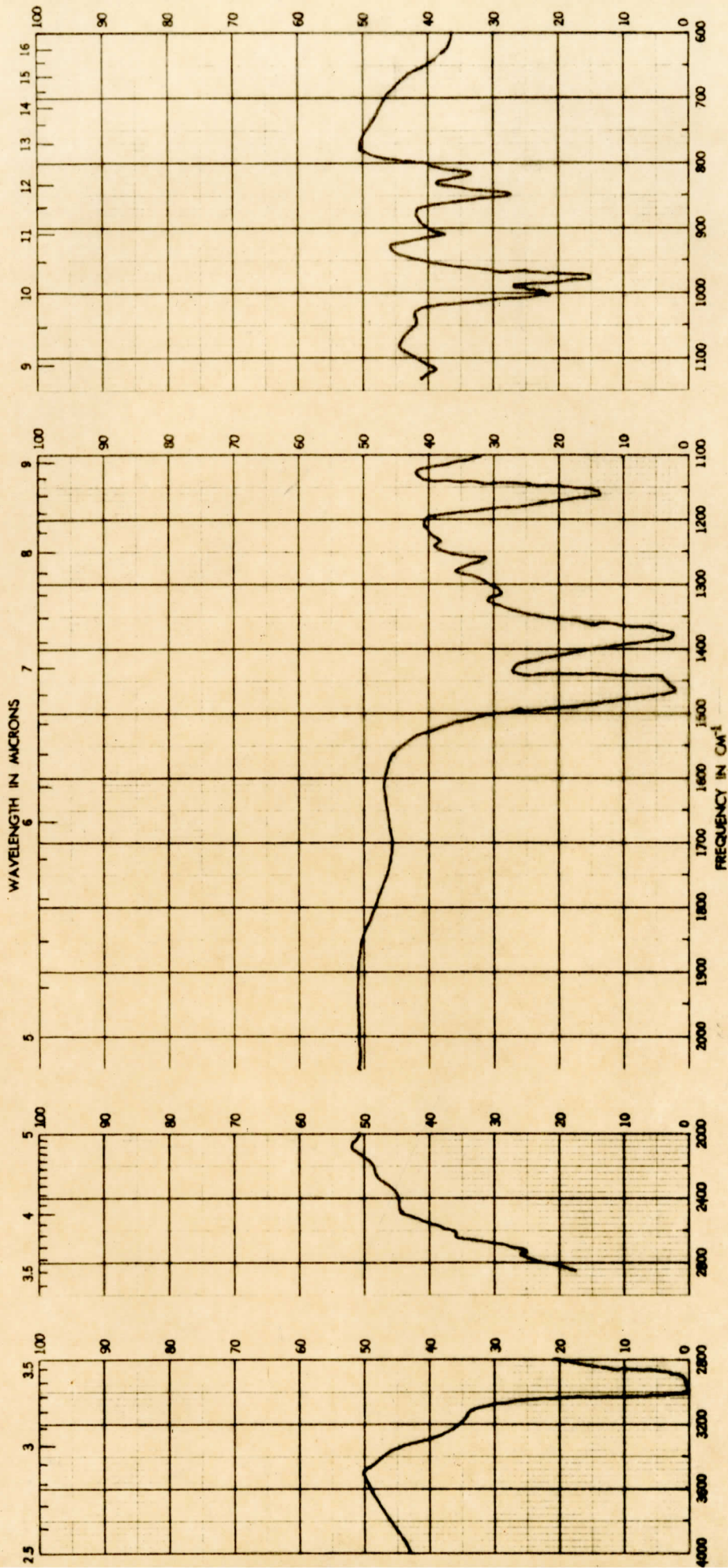
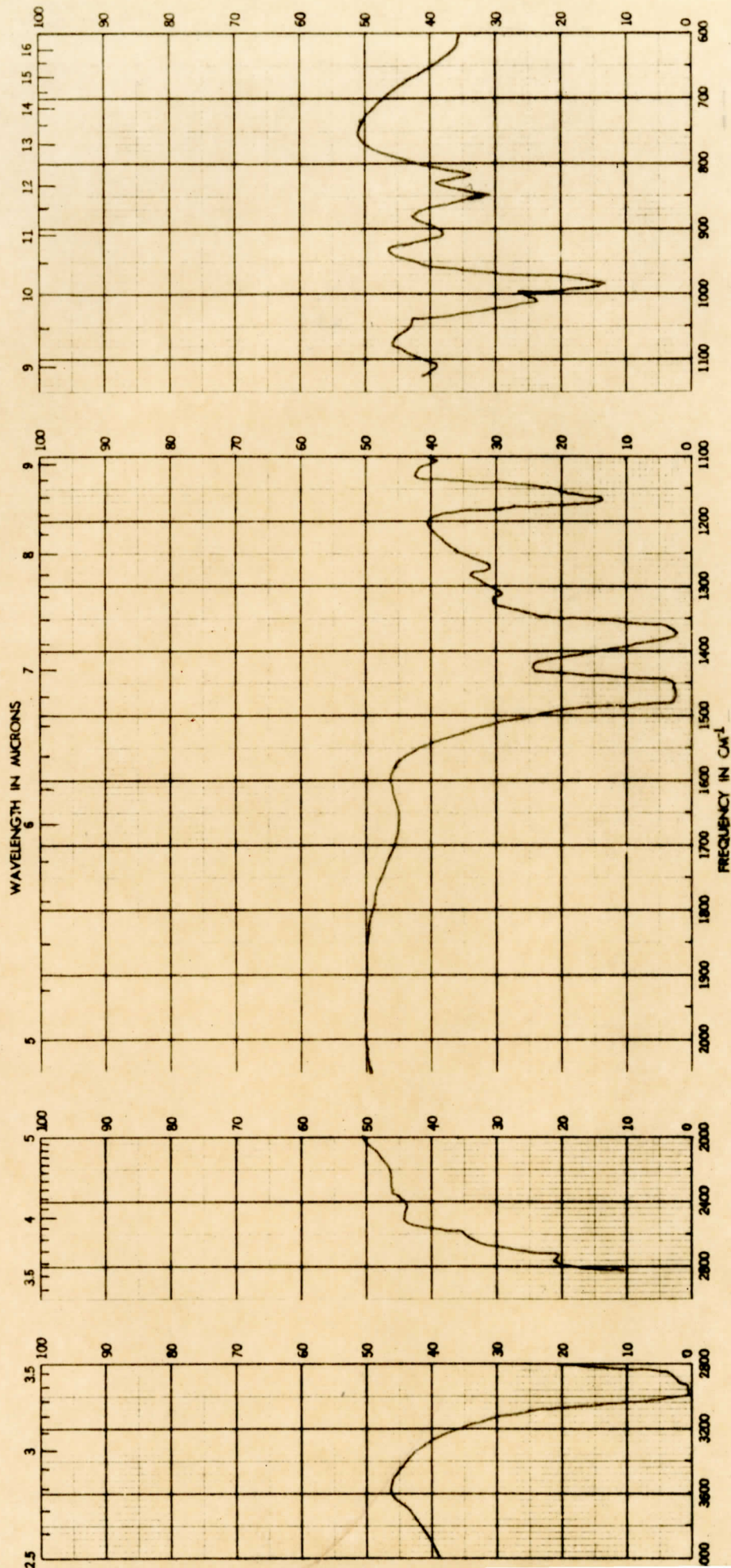


FIGURE 11

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $110 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER



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FIGURE 12

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE SAMPLE AT  $120 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

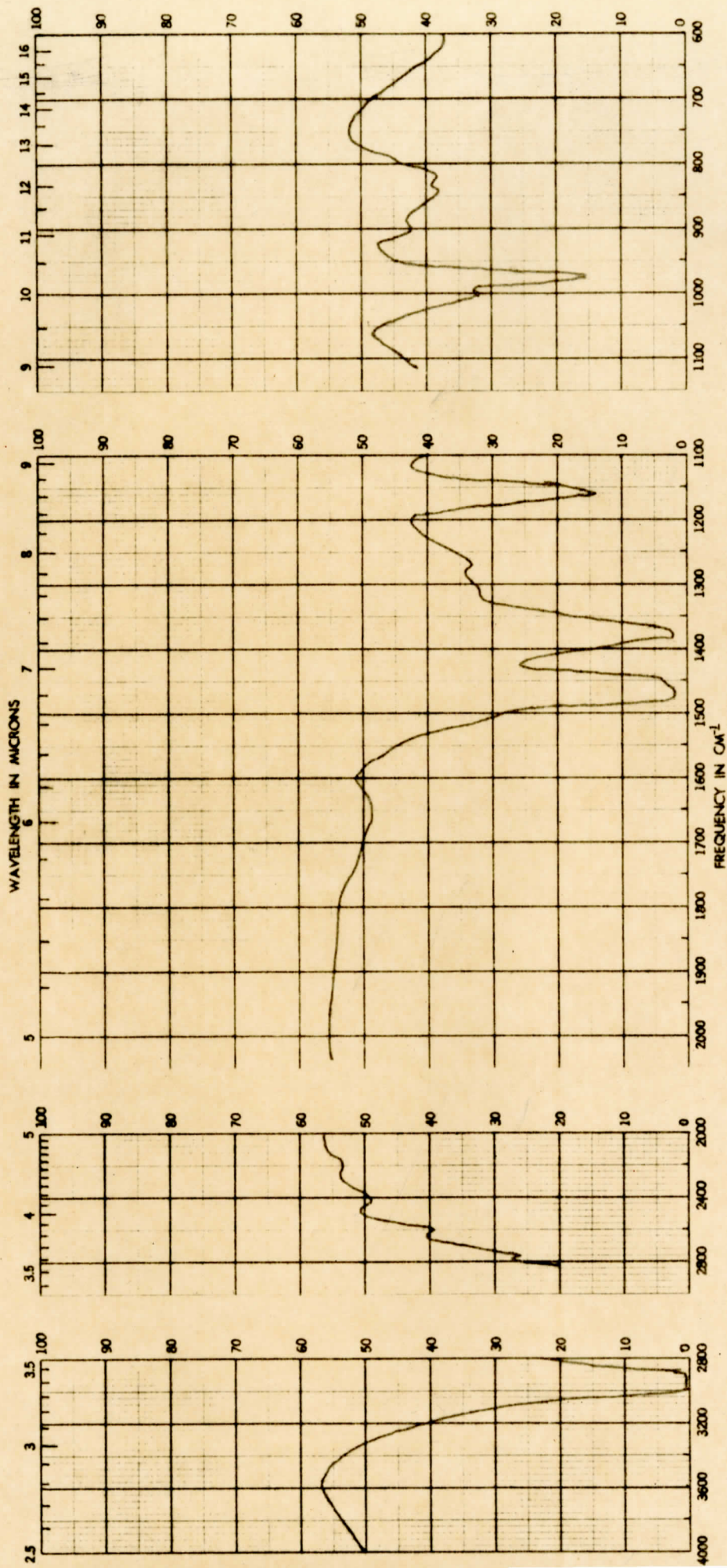


FIGURE 13

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $130 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER



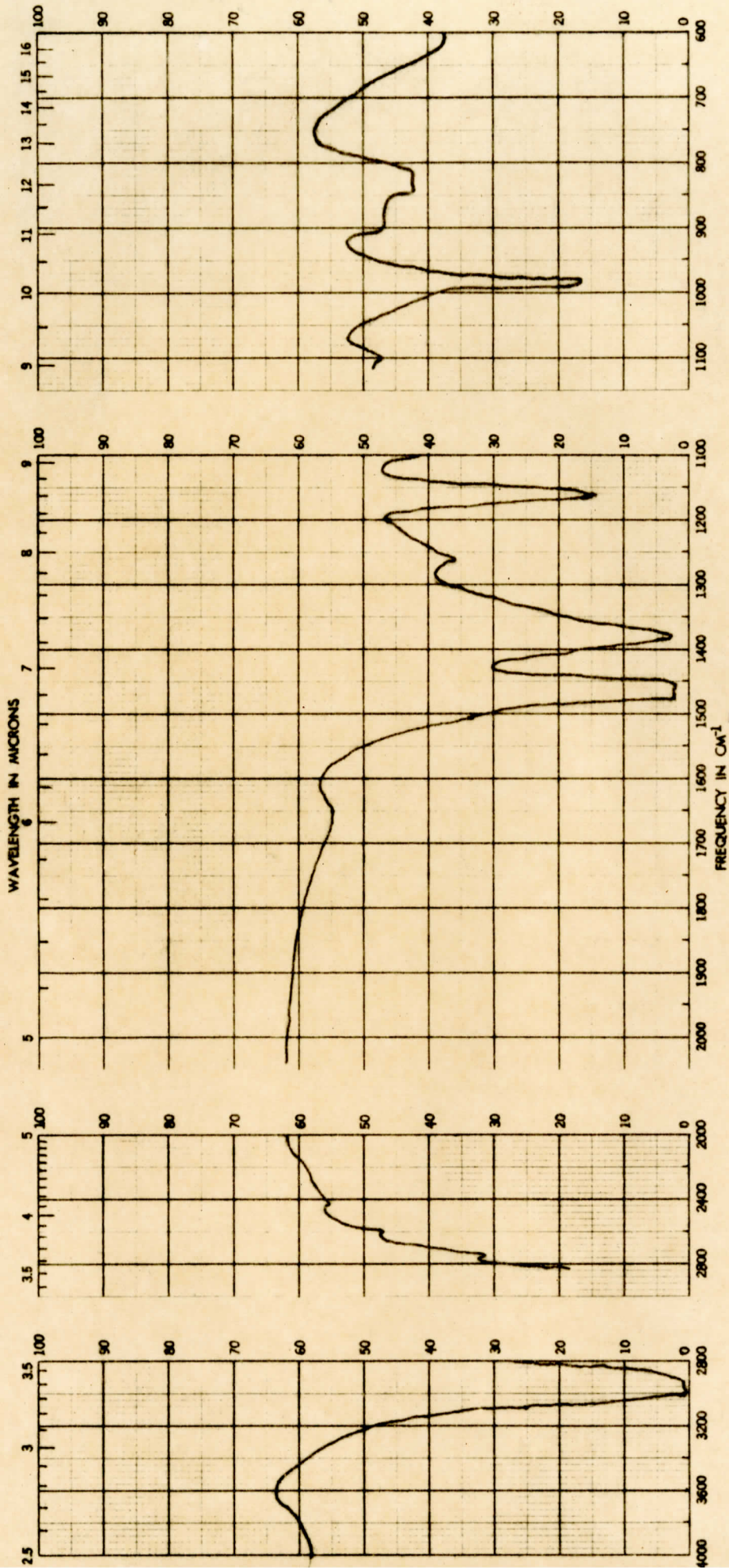


FIGURE 14

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $140 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

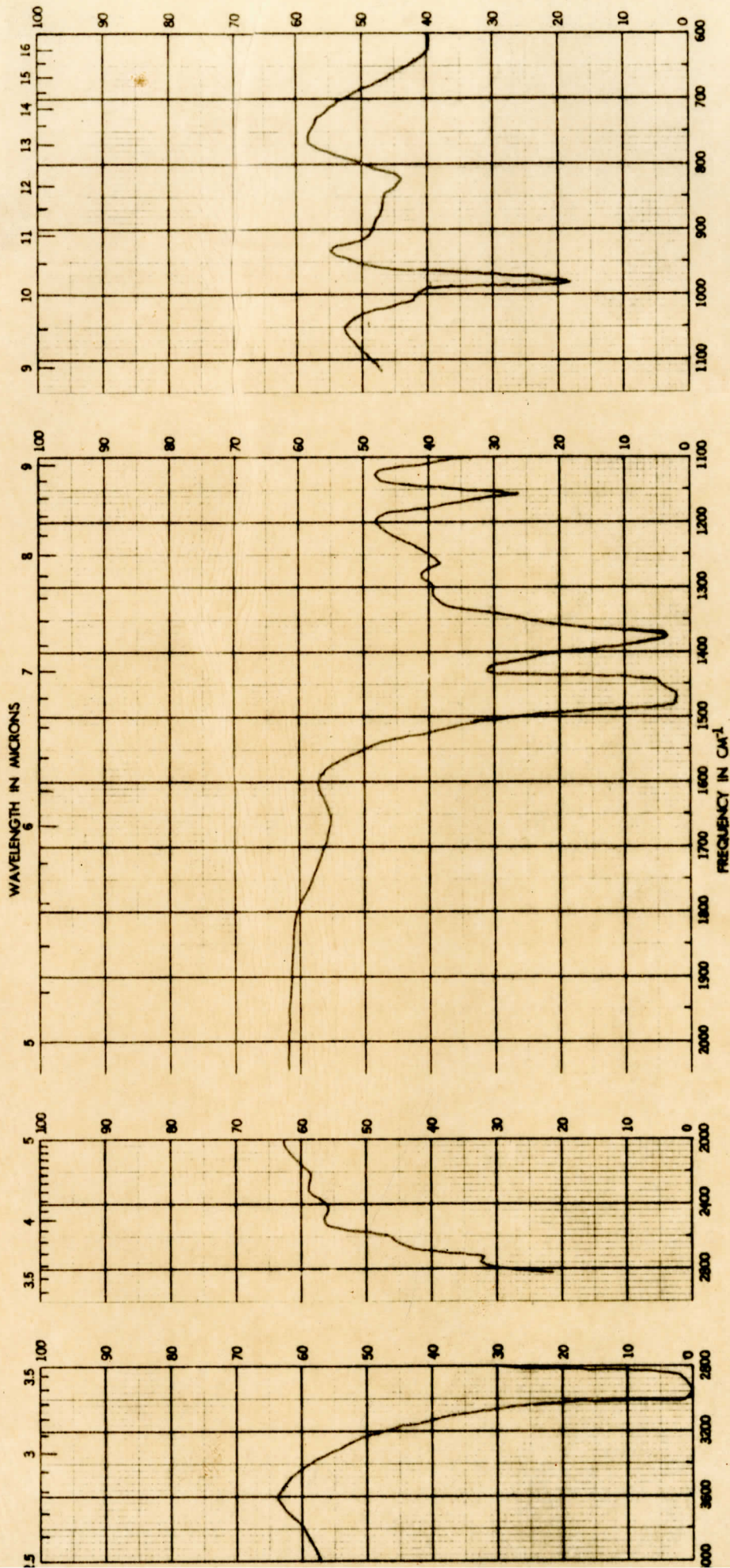


FIGURE 15

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $150 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

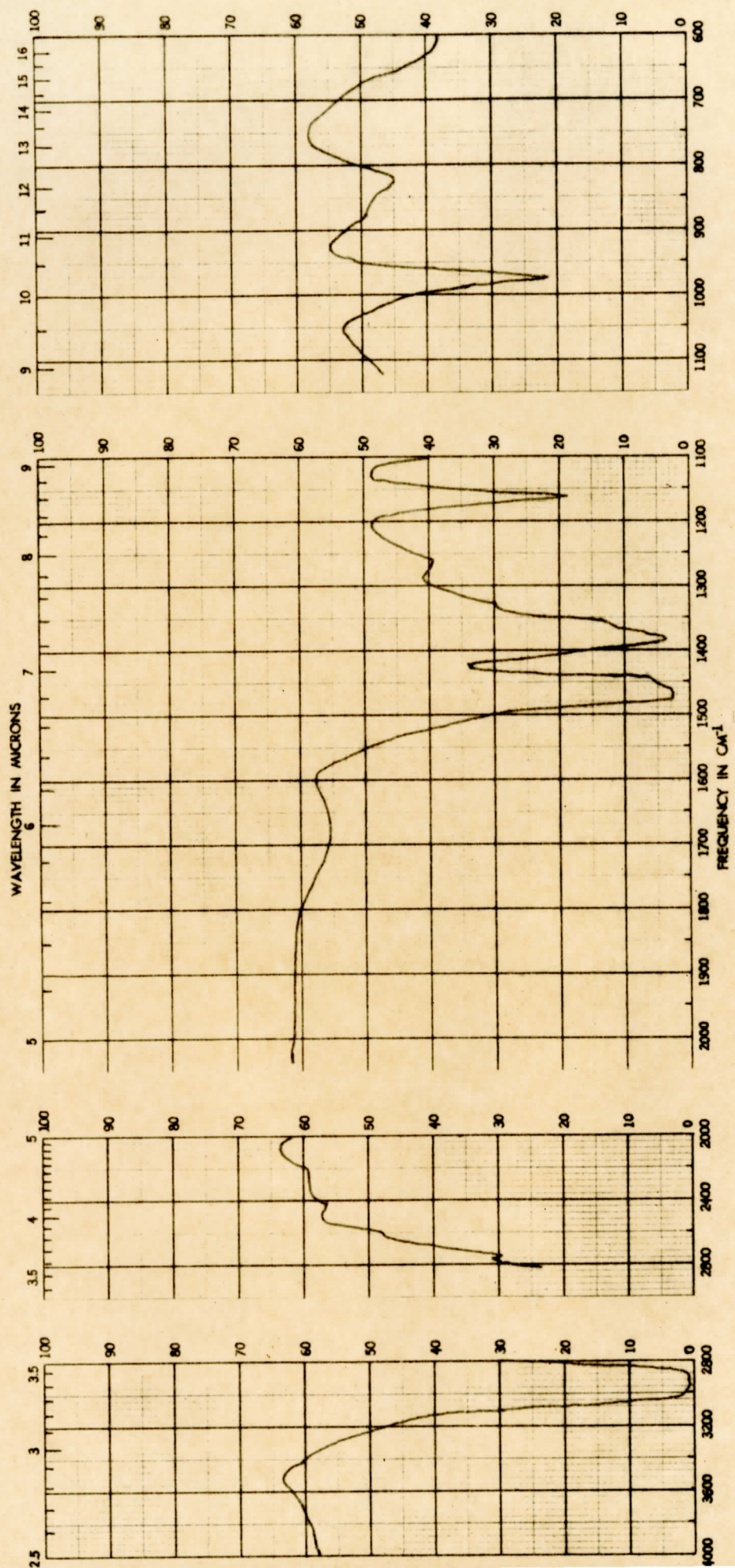


FIGURE 16

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE SAMPLE AT  $160 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

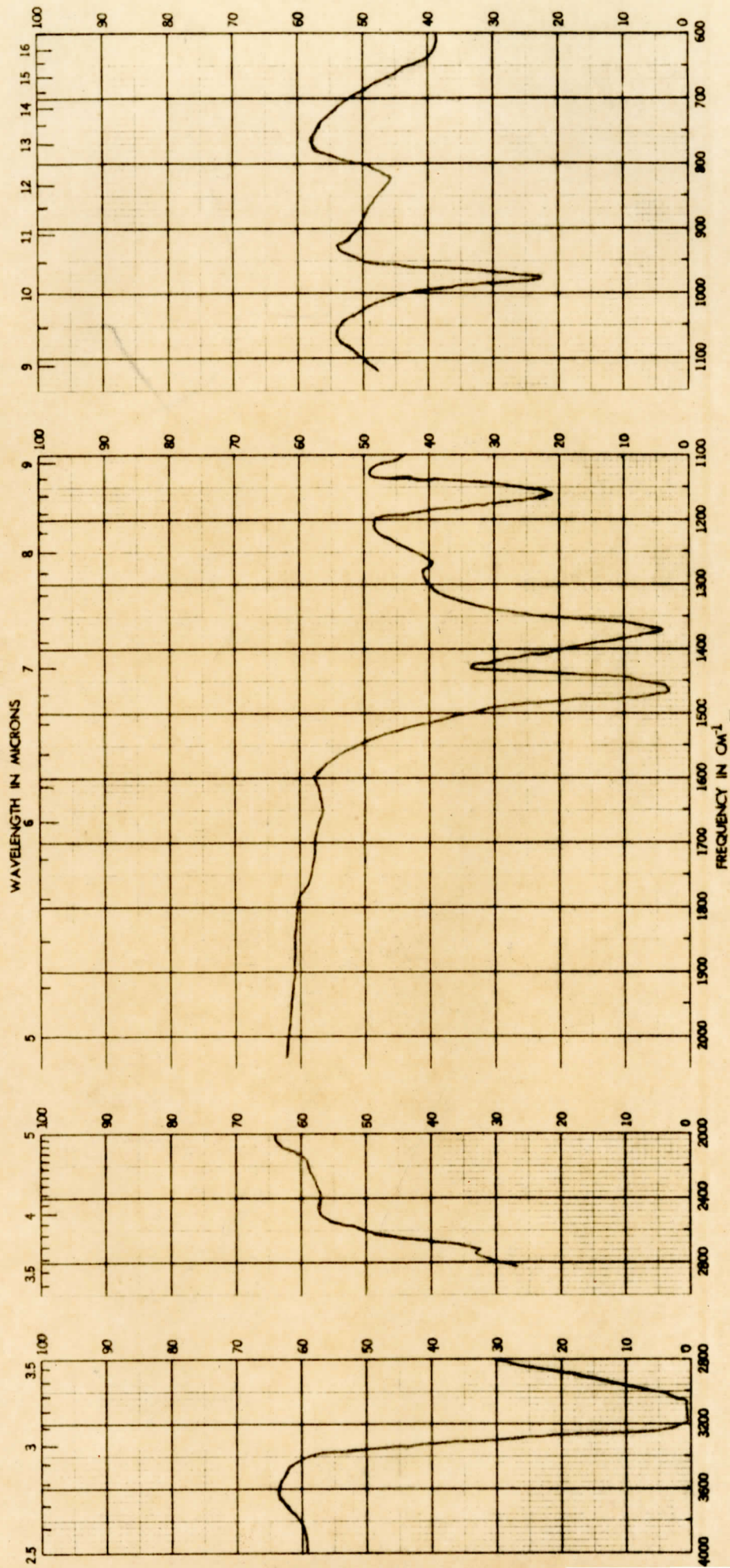


FIGURE 17

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $170 \pm 2^\circ$  C USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

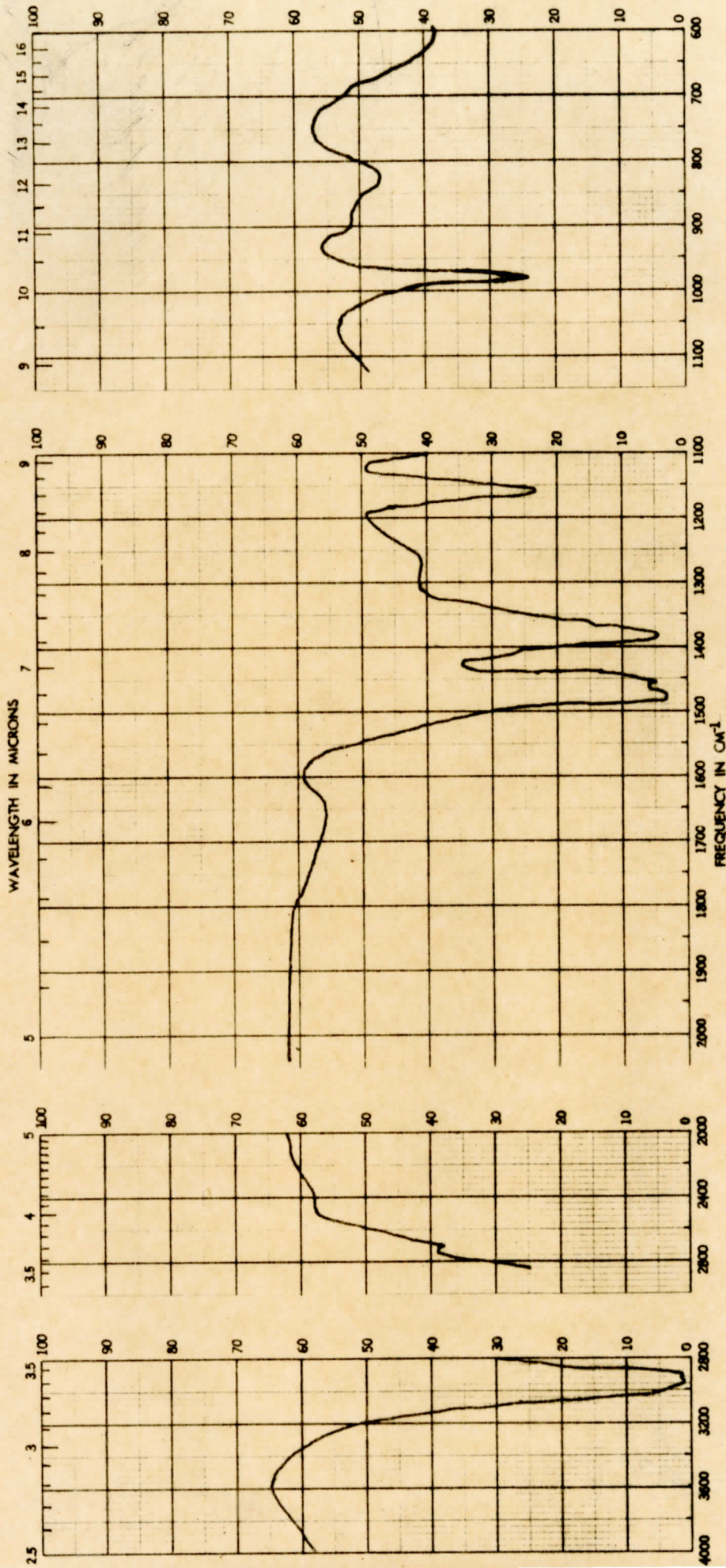


FIGURE 18

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE  
 SAMPLE AT  $180 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED  
 CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

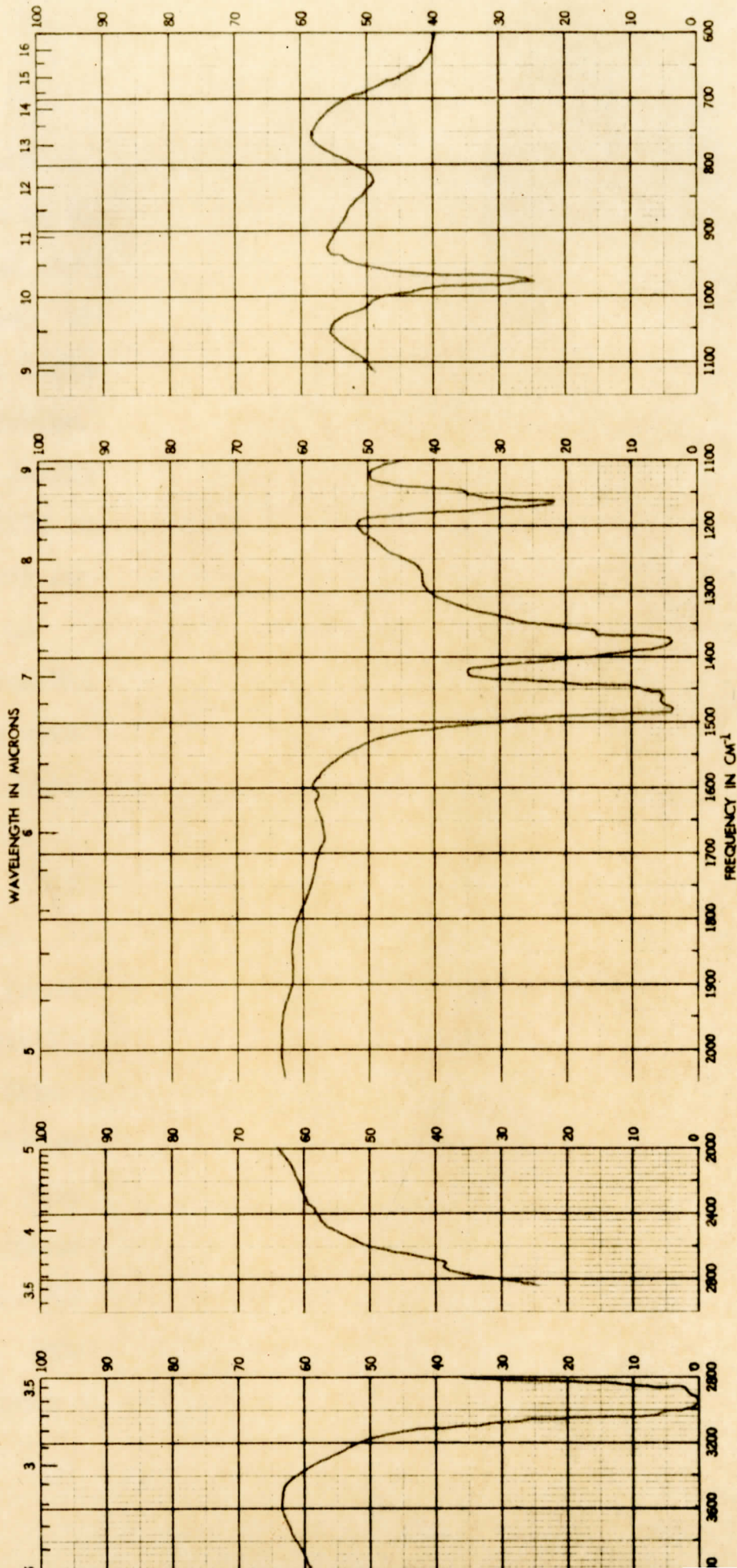


FIGURE 19

INFRARED SPECTRUM OF A 0.078 MM THICK ESCON-113 POLYPROPYLENE SAMPLE AT  $190 \pm 2^\circ \text{C}$  USING THE PERKIN-ELMER HEATED CELL AND THE BECKMAN IR-7 SPECTROPHOTOMETER

definition from this temperature up to  $160^{\circ}\text{C}$ . Notable are the bands at  $812\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$ ,  $902\text{ cm}^{-1}$ , and  $1002\text{ cm}^{-1}$  which become indistinguishable during the  $130^{\circ}\text{C}$ - $160^{\circ}\text{C}$  transition period. The infrared spectra of the film at  $170^{\circ}$ ,  $180^{\circ}$ , and  $190^{\circ}\text{C}$  indicates that there are no appreciable changes in the absorption bands during this period. Infrared bands which were fairly independent of changes in temperature included the  $1170\text{ cm}^{-1}$  band used as an internal thickness standard in this study. The  $812\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$ ,  $902\text{ cm}^{-1}$ , and  $1002\text{ cm}^{-1}$  infrared bands were among those which showed appreciable change with temperature indicating their association with the crystalline order of the polypropylene and, thus, their use in the measure of crystallinity in polypropylene.

Table XII gives the absorbance ratios for the  $812\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$ ,  $902\text{ cm}^{-1}$ , and  $1002\text{ cm}^{-1}$  infrared absorption bands as a function of temperature, and this relationship is shown graphically for the  $812\text{ cm}^{-1}$  absorbance ratio in Figure 20. From data and the plot, the polypropylene seems to have melted for all practical purposes, at about  $160^{\circ}\text{C}$ . The information given from this segment of the study also indicates the usefulness of the absorbance ratio as a measure of crystalline changes in polypropylene.

Other investigators have found similar results in most instances when polypropylene infrared spectra were investigated

TABLE XII

EFFECT OF TEMPERATURE ON SOME OF THE MORE PROMINENT  
INFRARED SPECTRAL BANDS OF A STEREOREGULAR  
POLYPROPYLENE FILM USING THE BECKMAN IR-7  
SPECTROPHOTOMETER AND THE PERKIN-ELMER  
HEATED CELL

Temperature	Absorbance ratios			
	812 $\text{cm}^{-1}$	843 $\text{cm}^{-1}$	902 $\text{cm}^{-1}$	1002 $\text{cm}^{-1}$
30°C	0.20	0.51	0.23	0.75
50°C	0.20	0.51	0.22	0.76
75°C	0.19	0.51	0.22	0.74
100°C	0.17	0.50	0.20	0.71
110°C	0.14	0.48	0.18	0.69
120°C	0.10	0.40	0.14	0.66
130°C*	0.05	0.20	0.10	0.53
140°C	0.02	0.15	0.07	0.21
150°C	0.01	0.12	0.07	0.16
160°C	0.01	0.11	0.06	0.14
170°C	0.00	0.10	0.03	0.14
180°C	0.00	0.10	0.02	0.14
190°C	0.00	0.11	0.02	0.14

\*An almost complete loss of band sharpness, and finally band identity, for all four bands occurred from this temperature up to 190°C.



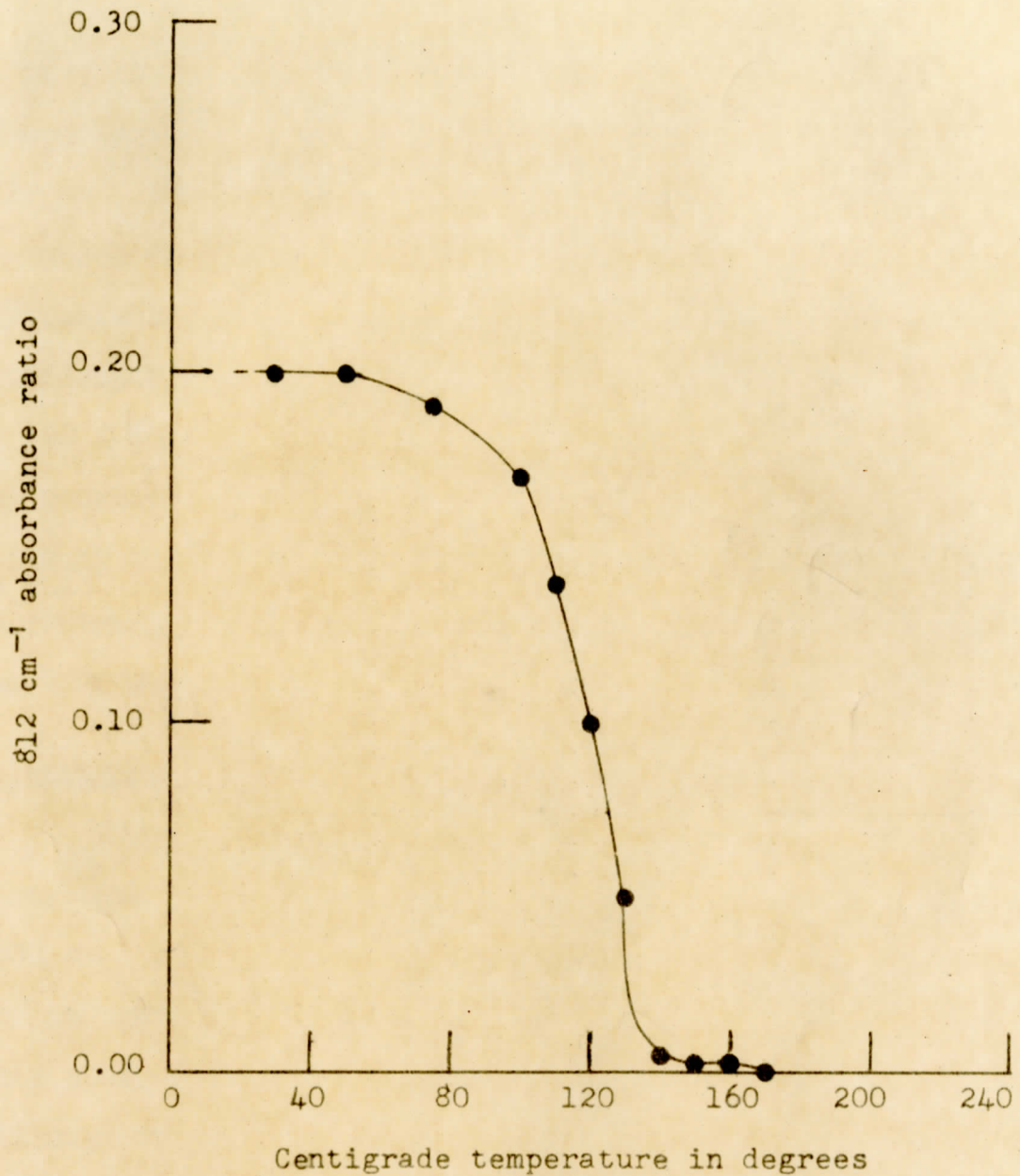


FIGURE 20

ABSORBANCE RATIO OF THE 812 CM<sup>-1</sup> AND 1170 CM<sup>-1</sup>  
INFRARED BANDS, AFTER BACKGROUND  
CORRECTIONS, AS A FUNCTION OF  
TEMPERATURE FOR THE ESCON-113  
POLYPROPYLENE FILM

at various temperatures (1)(8). Other investigators (1)(8) have reported that the  $1170\text{ cm}^{-1}$  band is displaced by the  $1159\text{ cm}^{-1}$  shoulder band indicating that the  $1159\text{ cm}^{-1}$  is an amorphous dependent band. The  $1159\text{ cm}^{-1}$  shoulder band, although difficult to resolve, was found to be present in both the room temperature infrared spectrum and the infrared spectrum at  $190^{\circ}\text{C}$  for the melted polypropylene film, and from observing the reactions of this band to temperature, it seems to be slightly related to the crystalline parts of the polymer since it showed slight decreases in absorbance with an elevation of the temperature.

#### Polypropylene Films of Different Densities

Figures 21, 22, 23, and 24 give the plots of the absorbance ratios for the  $812\text{ cm}^{-1}$ ,  $843\text{ cm}^{-1}$ ,  $902\text{ cm}^{-1}$  and  $1002\text{ cm}^{-1}$  absorption bands versus the specific volumes of the polypropylene films of varying densities prepared for this study. The data for these plots are given by Table XIII. Although in each plot there is some scatter of experimental points, an inverse relationship is found between the absorbance ratios and specific volumes in which the absorbance ratio appears to decrease linearly with increasing specific volume. Similar plots using the  $976\text{ cm}^{-1}$  band as the internal standard gave increased scattering of the points and, hence, they are not included. These relationships provide a measure

TABLE XIII

RELATIONSHIP BETWEEN THE ABSORBANCE RATIOS AT  
812  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ , 902  $\text{cm}^{-1}$ , AND 1002  $\text{cm}^{-1}$   
AND THE SPECIFIC VOLUMES FOR THE PREPARED  
POLYPROPYLENE FILMS

Sample	Specific volume	Absorbance ratios			
		812 $\text{cm}^{-1}$	843 $\text{cm}^{-1}$	902 $\text{cm}^{-1}$	1002 $\text{cm}^{-1}$
E-100	1.086 ml/g	0.26	0.71	0.28	0.78
E-101	1.082 ml/g	0.25	0.68	0.24	0.78
E-102	1.084 ml/g	0.22	0.76	0.26	0.79
E-103	1.095 ml/g	0.21	0.73	0.24	0.78
E-104	1.092 ml/g	0.21	0.69	0.23	0.76
E-105	1.086 ml/g	0.25	0.68	0.25	0.77
E-106	1.086 ml/g	0.25	0.73	0.25	0.82
E-107	1.110 ml/g	0.16	0.61	0.18	0.74
E-108	1.110 ml/g	0.25	0.60	0.22	0.70
E-109	1.080 ml/g	0.25	0.63	0.25	0.76
E-110	1.090 ml/g	0.28	0.69	0.29	0.80
E-111	1.080 ml/g	0.26	0.74	0.25	0.80
E-112	1.082 ml/g	0.24	0.76	0.27	0.76
E-200	1.092 ml/g	0.24	0.69	0.24	0.84
E-201	1.087 ml/g	0.24	0.70	0.26	0.76
E-202	1.092 ml/g	0.22	0.75	0.22	0.75
E-203	1.080 ml/g	0.24	0.73	0.26	0.80
P-100	1.084 ml/g	0.23	0.77	0.24	0.74
P-101	1.071 ml/g	0.28	0.70	0.29	0.82
P-102	1.071 ml/g	0.32	0.76	0.31	0.88
P-103	1.072 ml/g	0.29	0.67	0.29	0.86
E-300	1.101 ml/g	0.23	0.72	0.21	0.76
E-301	1.095 ml/g	0.22	0.67	0.27	0.78
E-400	1.110 ml/g	0.20	0.64	0.28	0.74
P-200	1.096 ml/g	0.21	0.61	0.25	0.73
E-500	1.073 ml/g	0.30	0.85	0.31	0.79
E-501	1.126 ml/g	0.11	0.53	0.22	0.70
E-600	1.108 ml/g	0.20	0.70	0.23	0.73
E-601	1.149 ml/g	0.04	0.42	0.16	0.61
E-602	1.155 ml/g	0.02	0.35	0.16	0.57
P-300	1.072 ml/g	0.29	0.82	0.31	0.87
P-301	1.069 ml/g	0.29	0.79	0.28	0.94

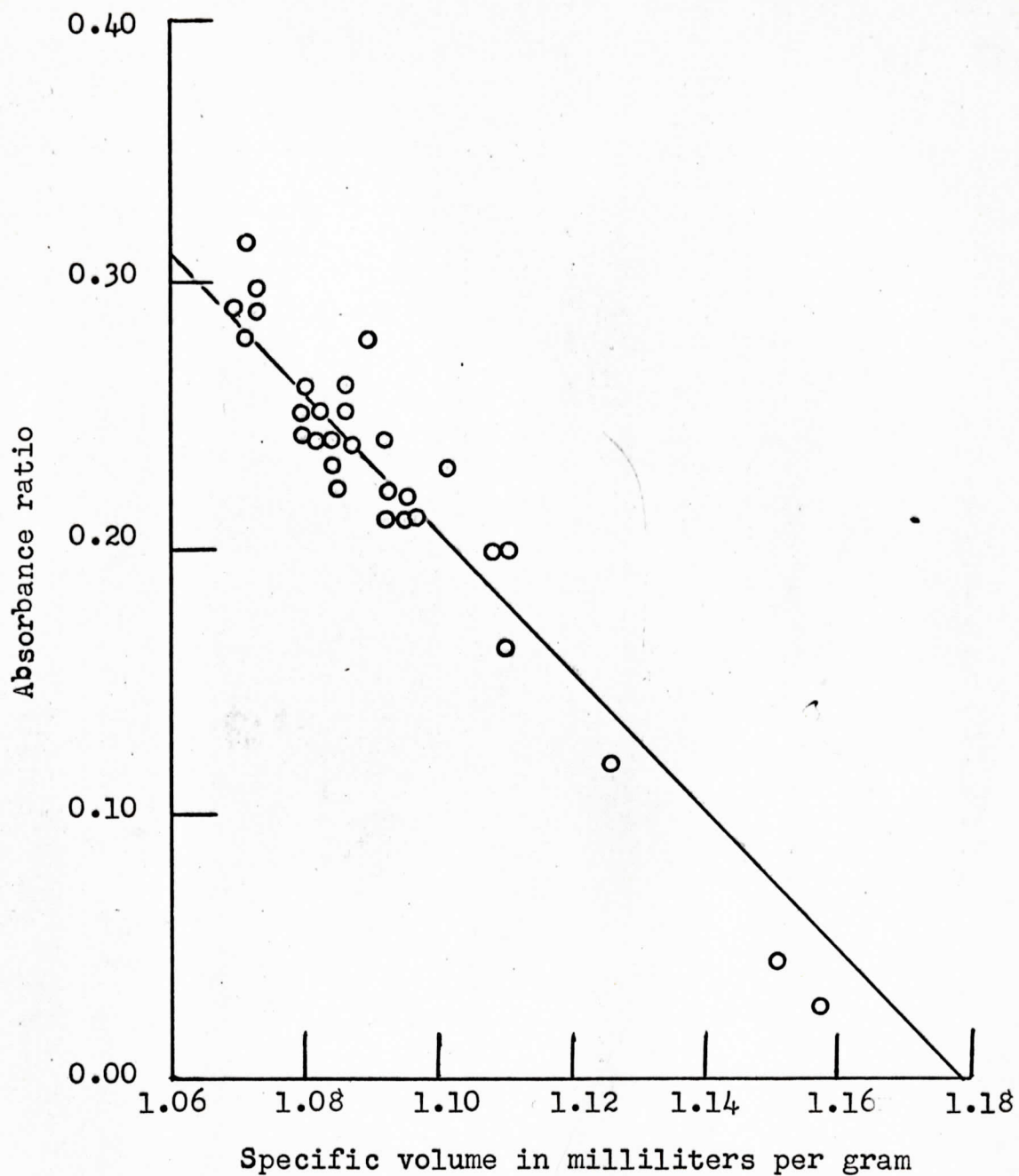


FIGURE 21

RELATIONSHIP BETWEEN THE  $812\text{ CM}^{-1}$  ABSORBANCE RATIO  
AND SPECIFIC VOLUME FOR THE POLYPROPYLENE FILMS

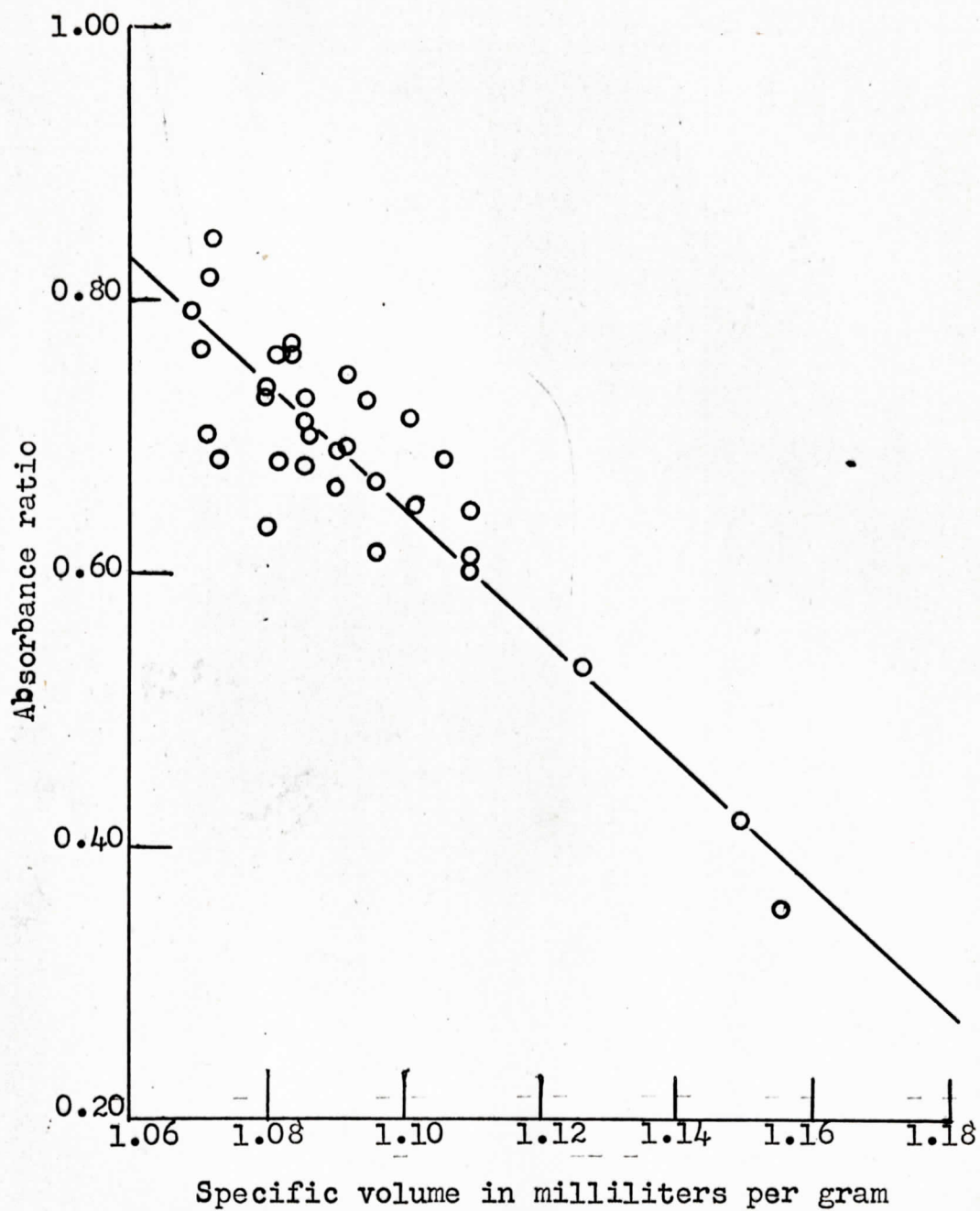


FIGURE 22

RELATIONSHIP BETWEEN THE  $843 \text{ CM}^{-1}$  ABSORBANCE RATIO AND SPECIFIC VOLUME FOR THE POLYPROPYLENE FILMS

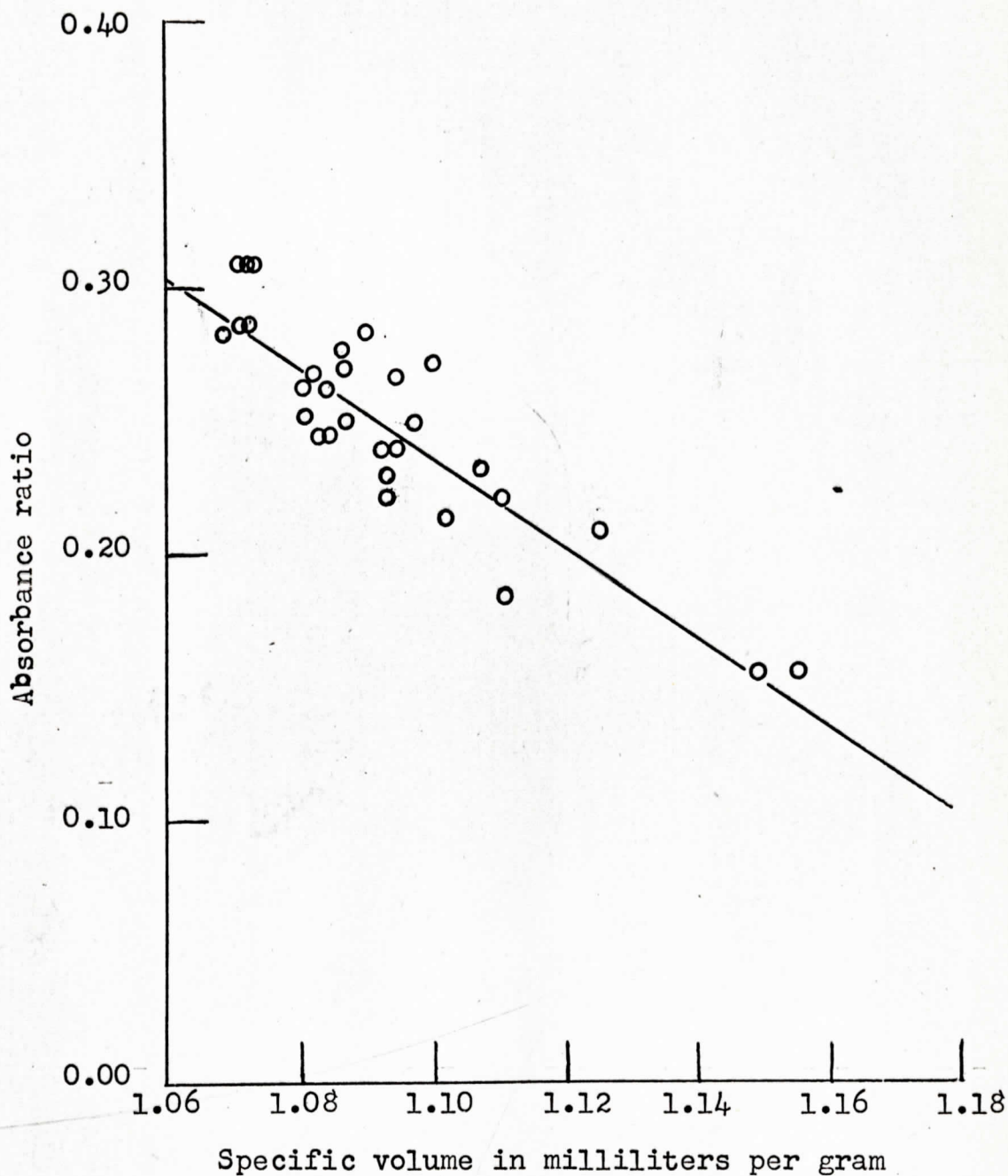


FIGURE 23

RELATIONSHIP BETWEEN THE  $902\text{ CM}^{-1}$  ABSORBANCE RATIO  
AND SPECIFIC VOLUME FOR THE POLYPROPYLENE FILMS

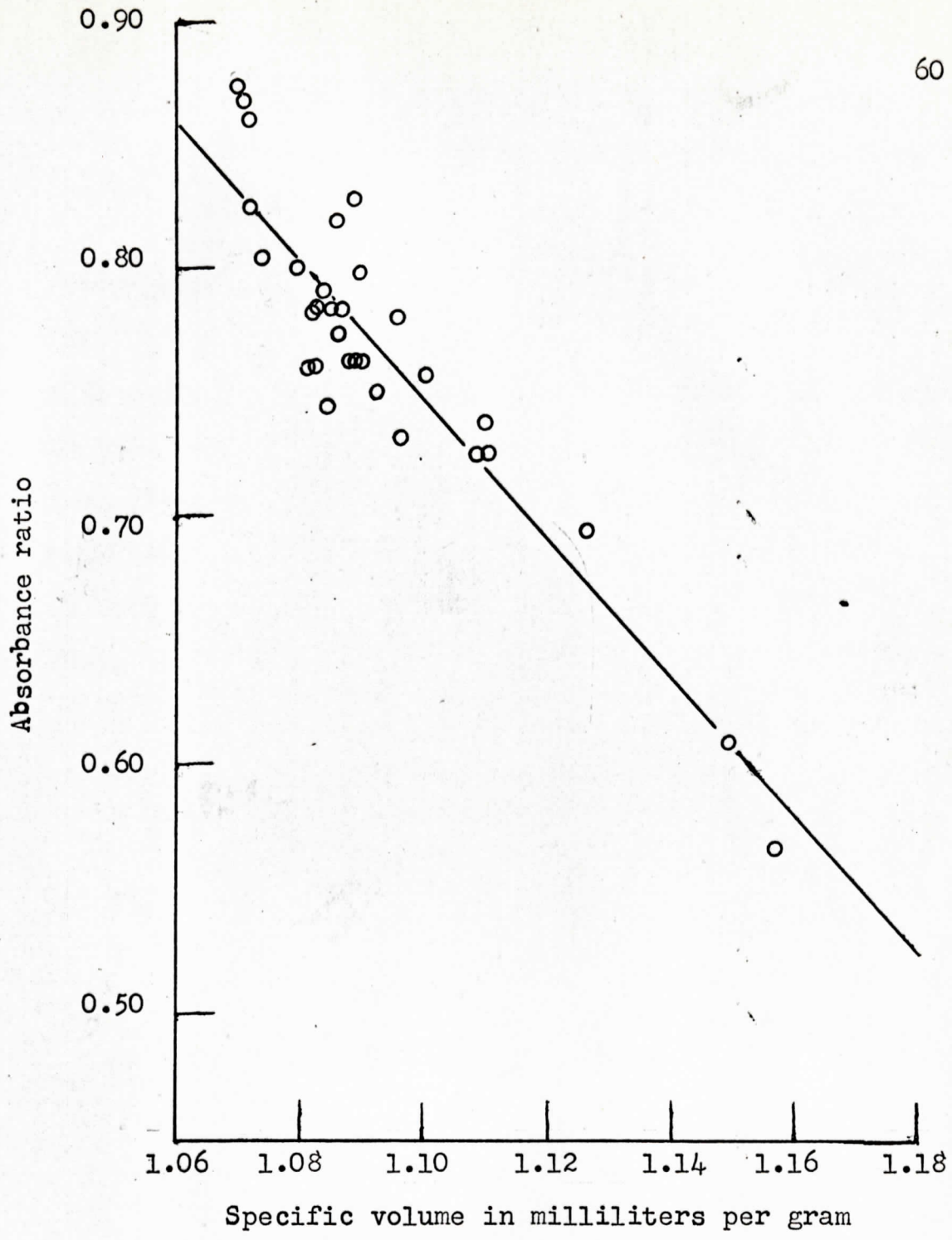


FIGURE 24

RELATIONSHIP BETWEEN THE 1002  $\text{CM}^{-1}$  ABSORBANCE RATIO AND SPECIFIC VOLUME FOR THE POLYPROPYLENE FILMS

of the crystallinities of the polypropylene films.

It is of interest to note, that the  $790\text{ cm}^{-1}$ , weak "amorphous" infrared band which is reported by Pokrovskii and Vol'kenshtein (15) as increasing in intensity with decreasing crystallinity was not detected in any film used in this study. However, all of the low density polypropylene films prepared in this study were found to contain a weak infrared band at  $725\text{ cm}^{-1}$  and a strong infrared band at  $1750\text{ cm}^{-1}$  which can not be completely explained at this time.



## CHAPTER V

### SUMMARY AND CONCLUSIONS

#### I. SUMMARY

Films of stereoregular polypropylene bulk polymers, Escon-113, Escon-125, Pro-fax 6501, and solvent soluble and insoluble fractions of these three, were prepared using various conditions for the pressed polymers, polymer melts, and polymer solutions. Films of different thicknesses, 0.035 mm to 0.195 mm, and different densities 0.866 g/ml to 0.935 g/ml, were obtained.

The densities of the bulk polypropylene samples and the prepared films were determined by flotation and gradient tube measurements. From these densities, it was possible to calculate the specific volumes and crystallinities of the prepared films.

Infrared spectra were obtained for a typical stereoregular polypropylene film and for films employed in thickness correlations with absorbance ratios using the Beckman IR-7 spectrophotometer. Infrared spectra were also obtained with a heated cell used in association with the IR-7 spectrophotometer for a polypropylene film heated to various temperatures. The information obtained from these studies was then applied to the infrared spectra obtained for the prepared polypropylene films having different densities. Absorption ratios for the

812  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ , 902  $\text{cm}^{-1}$ , and 1002  $\text{cm}^{-1}$  infrared absorption bands with the 1170  $\text{cm}^{-1}$  band used as an internal standard were established and used in plots of these ratios versus the specific volumes of the prepared films, as a measure of the crystallinities of the film.

## II. CONCLUSIONS

Crystalline sensitive and relatively crystalline insensitive infrared bands have been found which form the basis for, at least, a semi-quantitative method for assessing the crystallinity of stereoregular polypropylene by infrared spectroscopy.

It was further concluded from this study that the use of the 1170  $\text{cm}^{-1}$  infrared band of polypropylene as an internal standard and the subtraction of background absorbances from both the crystalline sensitive bands' absorbance and the internal standard's absorbance lead to the best correlation of intensity and crystallinity, via specific volumes.

In addition, it was concluded that previous interpretations that were given to the 1159  $\text{cm}^{-1}$  and 790  $\text{cm}^{-1}$  bands are inconsistent with the observations from this study.

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AN INVESTIGATION BY INFRARED SPECTROSCOPY  
OF THE CRYSTALLINE ORDER IN  
STEREOREGULAR POLYPROPYLENE

by

Earl Don Loos, Jr.

The purpose of this study was to prepare films of polypropylene polymer representing a wide density range, to investigate the infrared spectrum of polypropylene as a function of temperature, and to devise a method for correlating the specific volumes of polypropylene films with the intensities of certain crystalline sensitive absorption bands found in the infrared spectra of the films.

Polypropylene films were prepared using various pressing, melting, and dissolution procedures. The densities of the films were then measured using flotation and gradient tube methods.

Infrared spectra were obtained for a typical stereoregular polypropylene film and for films used in thickness-absorbance ratio correlations using the IR-7 spectrophotometer. Infrared spectra were also obtained with a heated cell used in association with the spectrophotometer for a polypropylene film heated to various temperatures. The infrared information, thus obtained, was applied to infrared spectra obtained for the prepared polypropylene

film of different densities. Absorbance ratios for the 812  $\text{cm}^{-1}$ , 843  $\text{cm}^{-1}$ , 902  $\text{cm}^{-1}$ , and 1002  $\text{cm}^{-1}$  infrared absorption bands using the 1170  $\text{cm}^{-1}$  band as an internal standard were correlated with the specific volumes of the films.

The study provided the following conclusions:

1. Crystalline sensitive and relatively crystalline insensitive infrared bands have been found which form the basis for, at least, a semi-quantitative method for assessing the crystallinity of stereoregular polypropylene by infrared spectroscopy;

2. The use of the 1170  $\text{cm}^{-1}$  infrared band of polypropylene as an internal standard and the subtraction of background absorbances from both the crystalline sensitive bands' absorbance and the internal standard's absorbance lead to the best correlation of intensity and crystallinity, via specific volumes;

3. It is concluded that previous interpretations given to the 1159  $\text{cm}^{-1}$  and 790  $\text{cm}^{-1}$  bands are inconsistent with the observations from this study.