Density, Crystallinity, and Heptane Insolubility in Isotactic Polypropylene*

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INTRODUCTION

An important property of isotactic polypropylene, indeed, of any sterically regular polymer, is its degree of isotacticity or isotactic content, which might be defined simply as the mole fraction of chain atoms which possess a specified steric configuration relative to their immediate neighbors along the chain. The degree of crystallinity of the solid polymer is obviously closely related to its isotactic content, since the steric regularity of the isotactic product confers a crystallizability not possessed by the atactic, amorphous material. For many purposes, a knowledge of the degree of crystallinity may be more useful than a knowledge of the specific structural features giving rise to crystallinity. Many mechanical and other physical properties are probably determined largely by the total fraction of crystalline material, irrespective of the types or combinations of crystallizable structures present.

Another index of isotactic content in polypropylene, used first by Natta and co-workers[1] is the amount of insoluble residue remaining after extraction with boiling *n*-heptane, or after successive extraction with heptane and other solvents, e.g., acetone and diethyl ether. This solubility criterion of isotacticity, widely used in this and other laboratories, stemmed from Natta's original observations[2,3] of marked solubility differences between isotactic and atactic linear polypropylenes.

This paper deals with the development of a density method for estimating percentage crystallinity in polypropylene and with the correlation between crystallinity (by density) and heptane insolubility. The density method is compared with x-ray and infrared methods of crystallinity determination. A limited amount of work was done to assess the influence of molecular weight (as judged by the intrinsic viscosity) on crystallinity and solubility.

The polymers studied were a variety of experimental polypropylenes, both whole and extracted, plus several commercial samples.

EXPERIMENTAL METHODS

Density

Density determinations were carried out in an ethanol/water density-gradient tube at 25.0 ± 0.1°C. Polypropylene samples about 10 mm.² in area were cut from films prepared for infrared measurements or were cut with a razor blade from polymer blocks used in the x-ray measurement. Densities were reproducible to within ± 0.001 g./cm.³.

The per cent crystallinity (by weight) was calculated from the observed density, additivity of specific volumes being assumed, on the basis of Natta's figures[4,5] for the density of completely amorphous and completely crystalline polypropylene, i.e., crystalline density = 0.936 g./cm.³; amorphous density = 0.850 g./cm.³.

The crystalline density is that calculated from the (postulated) unit cell dimensions, and the amorphous density is stated to be that of "amorphous linear polypropylene."[4] This latter figure agrees well with that derived from infrared and x-ray data, as discussed below.

X-Ray

The x-ray determination of percentage crystallinity was carried out by the method suggested by Natta et al.[4] The method is similar to that which has been used for polyethylene.[6] Polymer samples in the form of molded blocks or powders, approximately 1 × 2 cm. and about 1 mm. thick, were scanned by reflection with a Norelco recording diffractometer, the source being Ni-filtered CuKα radiation. Operating conditions were as follows.

Divergence slit:	0.5°
Receiving slit:	0.003 in.
Scatter slit:	0.5°
Scaler:	240 counts/sec.
Time constant:	8 sec.
Scanning speed:	2°/min.

The amorphous scattering curve was taken to lie between 9.0 and 28.0° 2θ, and the separation of amorphous scattering from the crystalline peaks was made by the method suggested by Natta et al.[4] The planimetered areas, I_1, I_2, I_3, I_4, lying under the four main crystalline reflections at 14.0, 17.0, 18.3, and the 20.9, 21.7° 2θ doublet, respectively, were used with a combined correction factor for each to calculate the (weight) percentage crystallinity, as follows:

$$\% \text{ Crystallinity} = \frac{3.06I_1 + 5.18I_2 + 6.89I_3 + 10.30I_4}{3.06I_1 + 5.18I_2 + 6.89I_3 + 10.30I_4 + 0.9(6.9)I_{\text{amorph}}} \times 100$$

The crystalline contributions of the weak diffractions at 25.3 and 28.2° 2θ were neglected. Samples which showed orientation effects, as judged by relative peak intensities or by observation of flat-plate diffraction patterns, were rerun as powders or in a rotating sample holder.

Infrared

The 8.60, 10.03, 11.13, 11.90, and 12.37 μ absorption bands in isotactic polypropylene, among others, weaken or vanish on passing from the highly crystalline polymer to an amorphous or molten one.[2,7] This is illustrated in Figure 1. Such "crystalline" bands thus provide a relative measure of the degree of crystallinity, if it is assumed that the infrared absorbance/unit thickness is proportional to the volume fraction of crystallinity.

A Perkin-Elmer Model 21 infrared spectrometer equipped with a NaCl prism was used. Polypropylene films 2 to 3 mils thick were prepared by compression molding at 140–170°C. for 2 min. at pressures of 5,000–10,000 psi followed by hot water cooling for 5 min. For a given polymer sample, the crystallinity could be altered by variations in the molding, quenching, and annealing technique, but this did not affect the absorption-density correlation, since both measurements were made on identical physical specimens.

Quantitative absorbance measurements were made at the bands at 10.03, 11.90, and 12.37 μ. The band at 8.60 μ was not suitable for measurement, since it is overlapped by the strong, crystallinity-insensitive band at 8.70 μ. The 11.13 μ band did not appear to correlate well with density, perhaps because of its strong dichroic effect. The band at 10.29 μ was used as an internal thickness calibration. The latter band is not entirely satisfactory as an internal calibration, since it weakens

slightly with decreasing crystallinity, but no other non-overlapping, crystallinity-insensitive bands of suitable intensity appear in the wavelength region of interest. A mechanical thickness measurement was difficult to make because of the soft, tacky nature of many films of low crystallinity.

It can be seen from Figure 1 that the three crystalline absorption bands in question, although weak, do not vanish entirely in the molten material (approximately 10°C. above the crystalline melting point). It is thus not feasible in every case simply to extrapolate the experimental absorbances to zero in order to establish the density of the amorphous material. The background scattering corrections have therefore been chosen arbitrarily on the basis of best reproducibility, and the following absorbance ratios were computed. For the bands at 10.03 and 11.90 μ

$$\text{Absorbance ratio} = \frac{A(\lambda) - A(10.90\,\mu)}{A(10.29\,\mu) - A(10.90\,\mu)}$$

For the band at 12.37 μ

$$\text{Absorbance ratio} = \frac{A(12.37\,\mu) - A(12.20\,\mu)}{A(10.29\,\mu) - A(10.90\,\mu)}$$

where $A(\lambda)$ is absorbance at wavelength λ. The calculated absorbance ratios were plotted against the densities. Estimates of the density of the completely amorphous polymer could then be obtained from absorbance ratios observed in molten samples.

A recent Russian paper[7] has reported the presence at 790 cm.$^{-1}$ (12.66 μ) of a weak "amorphous" band, i.e., one which increases in intensity as the crystallinity decreases. We have been unable to detect this band in amorphous specimens as thick as 100 μ.

Solubility and Intrinsic Viscosity

Natta has used a variety of extraction techniques which aim at indicating the isotactic content of a particular polymer preparation. The underlying assumption is, of course, that the crystallizable isotactic material will be less soluble than the uncrystallizable atactic material.[1] He has mentioned a variety of solvents for such extraction, including pentane and heptane, and a range of temperatures from room temperature to the unspecified temperature of a Soxhlet extraction
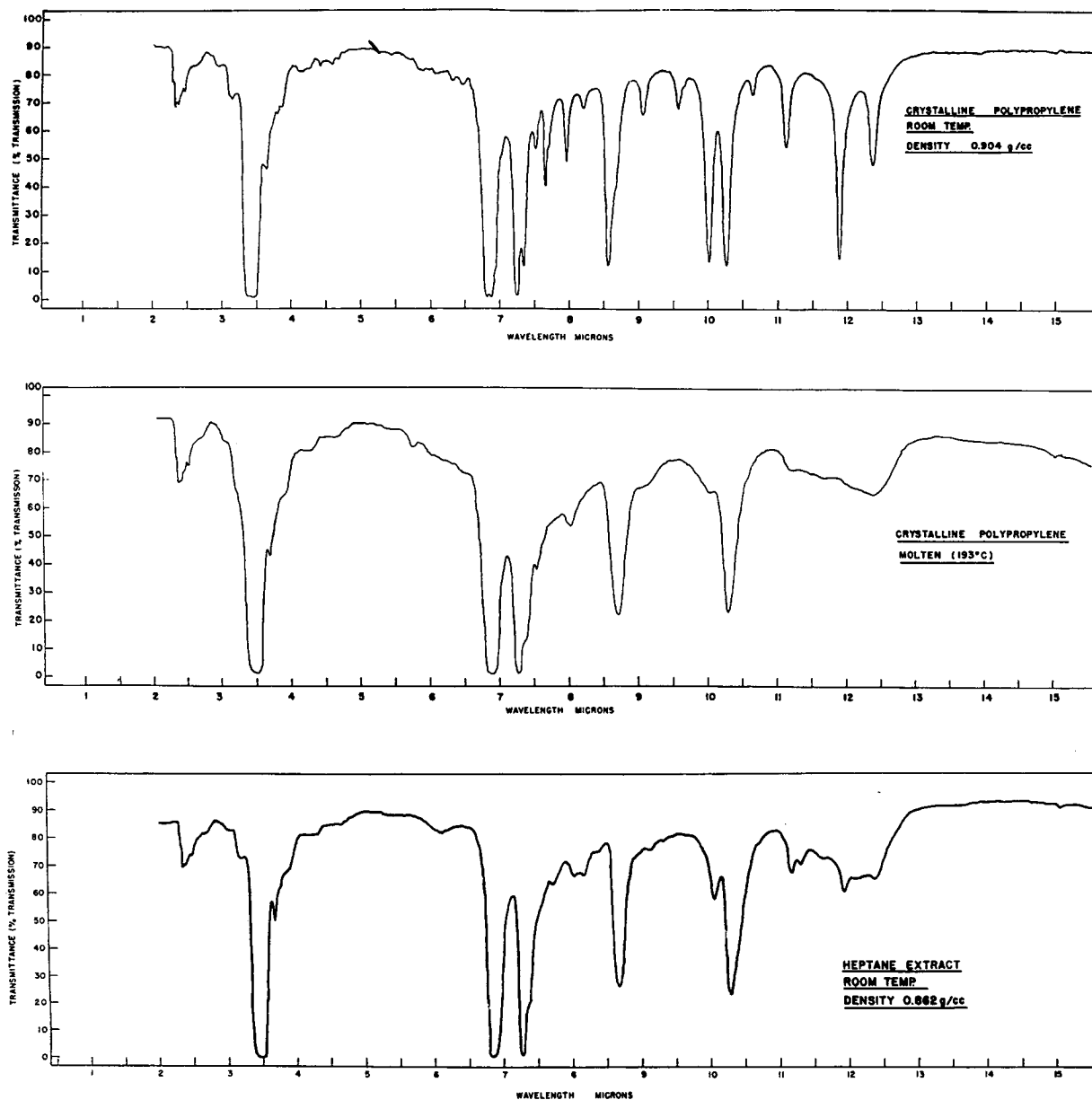
Fig. 1. Typical infrared spectra of crystalline and amorphous polypropylene.

thimble. Sequential extractions have also been described in which a polymeric material is successively extracted with acetone, diethyl ether, and heptane. It is a question of interest, only touched on in this paper, as to whether these techniques give the same result. Certainly the question may be raised as to whether any of these techniques indicates either the total crystallinity or the total isotactic content. The isotactic content certainly sets an upper limit to the possible crystalline content. That is, there cannot be more crystalline content than there is isotactic material. However, it is only rarely that a completely crystallizable polymer attains essentially complete crystallinity. The attainment of complete crystallinity depends upon the potential mobility of molecular segments and the time the material spends under crystallizing conditions—assisted thermally or by a liquid swelling agent. Depending on the polymer, the attainment of crystallinity is also influenced by the orientation of the polymer molecules. The foregoing set of considerations would tend to make insolubles by extraction lower than the isotactic content. On the other hand, in the extraction

TABLE I
Amorphous and Crystalline Densities of Polypropylene at 25.0°C.

| | Density g./cm.^{3} | | | | |
| | X-ray data | Infrared data | | | Litera-ture data |
		10.03 μ	11.90 μ	12.37 μ	
Amorphous	0.856	0.845	0.846	0.852	0.850[a]
					0.853[b]
Crystalline	~0.95		:		0.936[a]

[a] Reference 4.
[b] At 30°C., reference 5.

TABLE II
Heptane Insolubles, Intrinsic Viscosity, and Density of Unextracted Polypropylenes

Polymer	Insoluble residue, wt.-%	[η], dl./g.	Density, g./cm.^{3}
1	32	1.6	0.872[a]
2	45	6.0	0.874
3	51	3.0	0.884
4	54	4.2	0.890
5	55	5.3	0.883
6	56	4.3	0.878
7	56	4.3	0.878
8	59	4.9	0.885
9	60	4.6	0.876
10	64	5.4	0.883
11	65[b]	3.9	0.892
12	66	5.7	0.883
13	68	5.0	0.882
14	69	5.3	0.884
15	70[b]	3.0	0.895
16	70[b]	6.0	0.895
17	70[b]	9.6	0.897
18	75[b]	3.0	0.902
19	75[b]	7.0	0.891
20	76	8.0	0.889
21	80	7.4	0.892
22	81	7.9	0.895
23	83[b]	5.9	0.898
24	84[b]	4.0	0.900
25	90	9.4	0.905
26	91[c]	6.9	0.908
27	93[c]	9.4	0.905
28	93[c]	10.0	0.902

[a] Not measured; estimated from infrared data.
[b] After extraction with heptane only.
[c] After extraction with ether and heptane only.

process, large atactic molecules may either diffuse too slowly to escape from the solid phase or may actually be trapped in cavities in a crystalline region. Also, a molecule may have both isotactic and atactic portions. If this is the case, an isotactic portion may be part of a crystallite, and therefore bind the atactic portion, causing it to show up in the "insoluble" phase. Such considerations would make the residue of an extraction a high measure of crystalline content.

In this paper, we have attempted to deal with the actual crystalline content only, as we realize that the isotactic content will either equal or exceed it.

Most of the samples of Table II, in the form of finely divided powder, were extracted in a Soxhlet apparatus for 24 hr. each with (successively) boiling acetone, diethyl ether, and n-heptane. Insoluble residue is expressed as the percentage (by weight) remaining of an initial 10-g. sample. The samples were selected so that a broad range of solubilities and intrinsic viscosities was covered. The standard deviation of the determination was found to be 2.5%. Each value reported represents a single determination.

Three samples, as indicated in Table II, were prepared similarly except that no acetone extraction was made. Eight samples represent heptane extraction only.

Longer extractions did not reduce significantly the amount of residue. For the samples extracted with n-heptane alone, it was found that the results did not significantly differ from those obtained by multiple extractions.

Density and infrared measurements were made on films prepared from the whole polymers by compression molding at 160°C. The molding and cooling technique was held constant for this series of unextracted polymers and for residue samples derived from them. No further annealing was performed.

Intrinsic viscosities were measured with an Ostwald viscometer in decalin at 135.0°C. and at a polymer concentration of 0.1%. A relation between such viscosities and weight-average molecular weight has been suggested by Chiang.[8]

RESULTS AND DISCUSSION

Crystallinity (in weight per cent) obtained from x-ray data is plotted against specific volume (reciprocal density) in Figure 2. Extrapolation of the least-squares line to zero crystallinity leads to a density of 0.856 g./cm.^{3}. This figure is significantly greater than that derived from the infrared data, and equal to the lowest experimental density observed during this work, that of ether and heptane extracts of isotactic polypropylene. These figures indicate that the x-ray method may fail to measure the contribution of small or imperfect crystallites at small but finite crystallinities. The less reliable extrapolation to 100% crystallinity leads to a
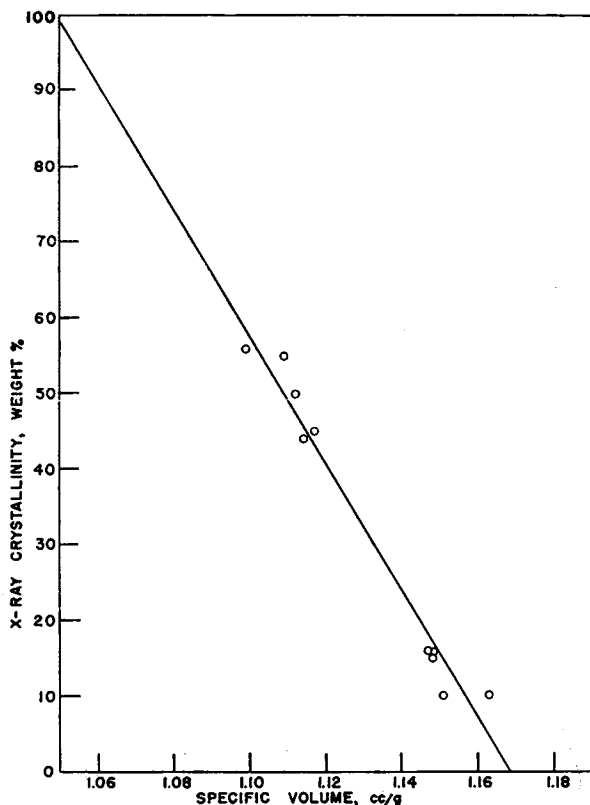
Fig. 2. Crystallinity by x-rays vs. specific volume for polypropylene.

Fig. 3. Correlation of infrared absorption at 10.03 μ with density for polypropylene.

density of 0.95 g./cm.³, in fair agreement with the assumed crystalline density of 0.936 g./cm.³.

In Figures 3, 4, and 5 are shown the infrared absorbance ratios plotted against density. The linearity of these plots shows that the infrared absorption of these bands and the density depend on crystallinity in the same way. The x-ray data indicate that the dependence is almost certainly linear, at least up to densities of 0.91 g./cm.³. The best molten polymer spectra (observed at 10–15°C. above the melting point) showed absorbance ratios of 0.17, 0.11, and 0 for the 10.03, 11.90, and 12.37-μ bands, respectively. These values correspond to "amorphous" densities of 0.845, 0.846, and 0.852 g./cm.³, respectively. The infrared values, collected in Table I, thus show reasonably good agreement among themselves, and good agreement with Natta's figure[4] of 0.850 g./cm.³. The latter figure may therefore be used with some assurance as one end-point of the crystallinity scale. (The infrared method tacitly assumes, of course, that the specific absorption coefficients are equal in the molten and room temperature polymer.) A revision in the calculated 100% crystalline density would then
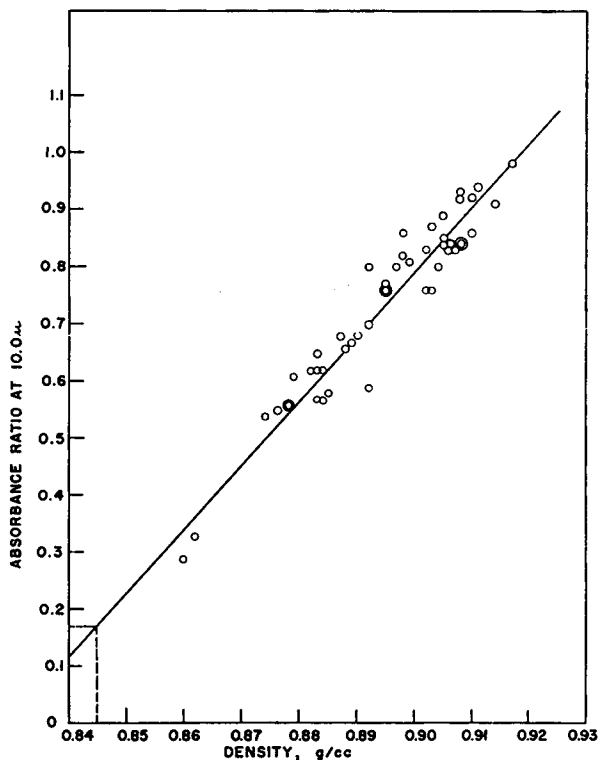

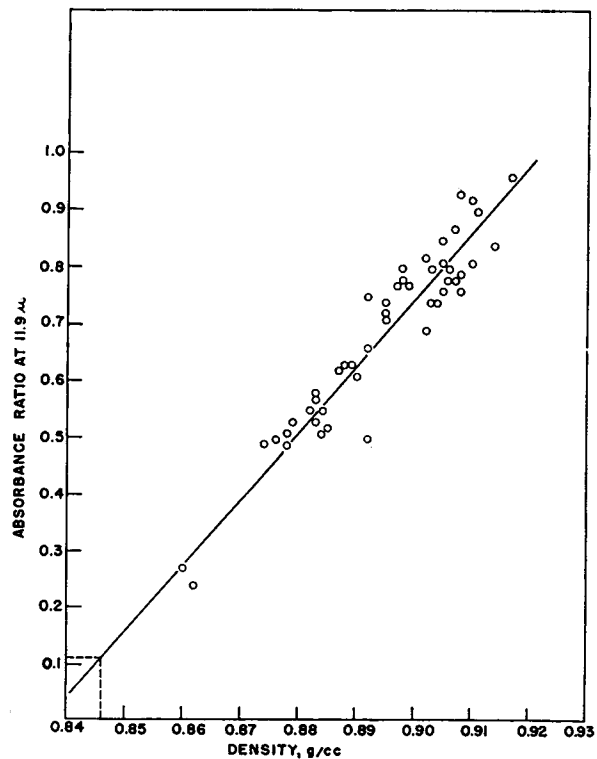Fig. 4. Correlation of infrared absorption at 11.90 μ with density for polypropylene.

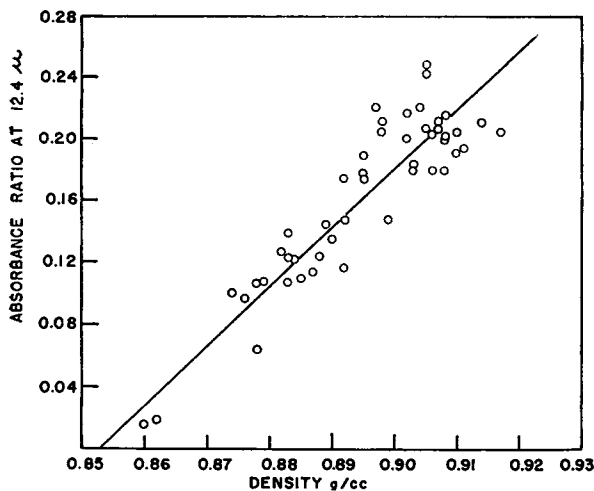Fig. 5. Correlation of infrared absorption at 12.37 μ with density for polypropylene.

Fig. 6. Correlation of amount of insoluble residue with density for polypropylenes of different intrinsic viscosities (I.V.).

affect only the slope of the crystallinity-specific volume line. Such x-ray densities are commonly accurate to perhaps ±0.04 g./cm.³ because of the combined uncertainties in the unit cell parameters.

The solubility-density data for 28 unextracted polypropylenes are given in Table II and shown graphically in Figure 6. Table III lists the results for a number of heptane-insoluble residues and compares them with the properties of the parent polymers. The points in Figure 6 have been segregated into ranges of intrinsic viscosity, and the solid lines represent an attempt to connect points of approximately equal intrinsic viscosity. Intrinsic viscosities were not available for the residues. The crystallinities in Table III were calculated from the density. Also shown in Figure 6 is a line relating density to per cent crystallinity for values of 0.850 and 0.936 g./cm.³ for amorphous and crystalline densities, respectively. It is apparent that for all samples the proportion of insoluble residue exceeds the corresponding percentage crystallinity as derived from the density
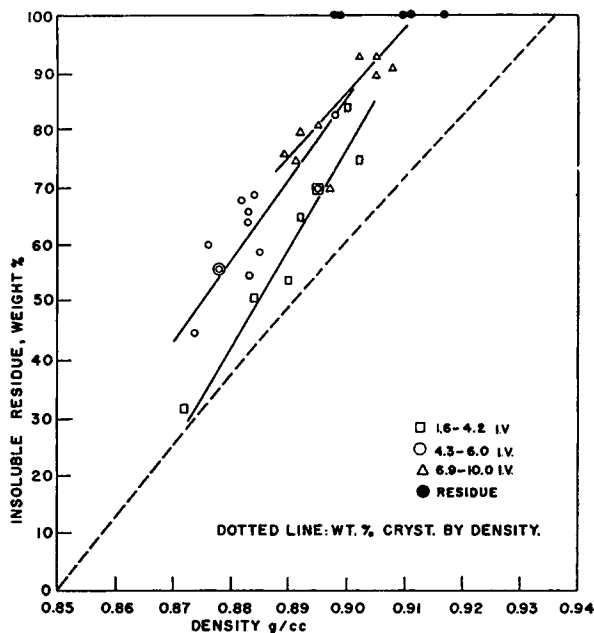
determination. It is clear from Figure 6 that there is a rough, approximately linear correlation between insoluble residue and density of unextracted polymer. To a crude approximation, the polymer may be regarded as consisting of two fractions only, one being heptane-insoluble and having a density 0.910 g./cm.³ (72 wt.-% crystallinity), the other being heptane-soluble with density 0.850 g./cm.³ (zero crystallinity).

However, it is apparent from the scatter of points that other factors influence the relationship. If the points are segregated (somewhat arbitrarily) into ranges of intrinsic viscosity as shown, there appears to be a fairly distinct, separate correlation for each intrinsic viscosity range. Thus, at constant $[\eta]$, an increase in crystallinity (density) corresponds to an increase in heptane insolubility.

TABLE III
Properties of Insoluble Residues Compared to Properties of Original Polymer

Original polymer	Residue, wt.-%	Original $[\eta]$, dl./g.	Density of original polymer, g./cm.³	Density of residue, g./cm.³	Crystallinity of residue, wt.-%
1	26[a]	1.6	0.872[b]	0.898	58
7	56	4.3	0.878	0.899	59
15	70[a]	3.0	0.895	0.911	73
16	70[a]	6.0	0.895	0.910	72
17	70[a]	9.6	0.897	0.917	80

[a] Extracted with heptane only.
[b] Not measured; estimated from infrared data.

A similar result has been observed recently for polyethylene:[9] for polyethylene fractions at constant molecular weight, the more crystalline fractions were less soluble in xylene. Within the fractions of any one sample, the increased solubility expected of those fractions with lower crystallinities was outweighed by their higher molecular weight. This result was true for both ordinary and high-density (linear) polyethylene.

Several samples in Table II and Figure 6 do not follow the correlations of the majority, e.g., numbers 16 and 17. Since the densities of these particular samples correlate closely with the infrared data, it is unlikely that the densities themselves are in error. The heptane insolubility and intrinsic viscosity data refer to the original polymer flake, while the densities and infrared data refer to films molded at 160°C. from the original polymers. It is known that the molding operation changes slightly the density of the original polymer, increasing or decreasing it by as much as 0.005 g./cm.[3]. This factor may account for some of the scatter of points.

Another indication that the whole polymer is not simply a mixture of two well-defined components is given by the results of Table III, where the densities of the insoluble residues are compared to the properties of the parent (whole) polymers. These rather limited data show, instead of a constant residue density independent of original polymer density or per cent residue, that the residue density increases with the density of the parent polymer. It is of interest to note that the density of three residues is equal to or greater than 0.910 g./cm.[3], the density attributed to the insoluble polymer, while the remaining densities lie below this value. This shows that heptane insolubility does not uniquely define the crystallinity of the residue, the range being 58–80% crystallinity.

In summary, a linear correspondence has been found for the crystalline content of polypropylene samples by x-ray diffraction, infrared absorbance, and density. The heptane-insoluble residues over a crystallinity range for the original polymers of 28 to 70% are, in every instance, higher than the crystalline content derived from the density measurement. The increase in residue with intrinsic viscosity indicates the dependence of solubility on molecular weight. As it appeared that the extractions had come to equilibrium, it may be conjectured (if the translation of density to crystallinity is correct) that much atactic material remains in the insoluble residue. This atactic ma-

terial probably interferes with the development of crystallinity (as seen from the different crystalline content of residues of different initial crystallinity), and is apparently bound to the crystallized material, perhaps by a mixture within the same molecule of isotactic and atactic order or by entrapment of atactic molecules within crystallite voids.

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Synopsis

Measurements of the density of a large number of experimental isotactic polypropylenes have shown that the specific volume is linearly related to per cent crystallinity as determined from x-ray data. The density is also linearly related to the absorbance of certain absorption bands in the infrared spectrum of isotactic polypropylene. The infrared data allow a determination of the density of the amorphous polymer which is in good agreement with literature values and with a value determined from the x-ray data by extrapolation to zero crystallinity. It is found that there is a rough, approximately linear correlation between crystallinity (by density) of unextracted polypropylene and the per cent insoluble residue remaining after extraction with boiling n-heptane or after successive extraction with other solvents and heptane. In all instances, the amount of residue exceeds the crystalline content. The crystallinity-insolubility relationship is influenced by molecular weight (as judged by intrinsic viscosity). An increase in crystallinity at constant $[\eta]$ corresponds to an increase in insolubility; at constant crystallinity, a larger $[\eta]$ corresponds to greater insolubility. In terms of density, the unextracted polymer may not be regarded as simply a mixture of two well-defined components, since the density of insoluble residue increases with the density of the whole polymer.

Résumé

Des mesures de densité d'un grand nombre de polypropylènes expérimentaux isotactiques montrent que le volume spécifique est lié linéairement au pourcentage de cristallinité évalué aux rayons-x. Cette densité est aussi

liée linéairement à l'absorbance de certaines bandes dans le spectre infra-rouge du polypropylène isotactique. Des données infra-rouges fournissent une détermination de la densité du polymère amorphe que est en bon accord avec les valeurs de la littérature, et avec les valeurs déterminées au moyen des rayons-x par extrapolation à une cristallinité nulle. On a trouvé une relation approximativement linéaire, entre la cristallinité (par densité) du polypropylène non purifié e tle pourcentage de résidu insoluble que reste après extraction pas le n-heptane bouillant, ou après des extractions successives avec d'autres solvants et de l'heptane. Dans tous les cas, la quantité de résidus dépasse le pourcentage de cristallinité. Le rapport de la cristallinité à l'insolubilité est influencé par le poids moléculaire (déterminé par viscosimétrie). Une augmentation de cristallinité à viscosité spécifique constante correspond à une augmentation d'insolubilité. À cristallinité constante, une viscosité intrinsèque plus grande correspond à une insolubilité plus grande. En termes de densité, le polymère non purifié ne peut pas être regardé comme un simple mélange de deux composés bien définis, puisque la densité du résidu insoluble augmente avec la densité du polymère total.

Zusammenfassung

Dichtemessungen an einer grossen Zahl für experimentelle Zwecke hergestellter, isotaktischer Polypropylene haben gezeigt, dass das spezifische Volumen in einer linearen Beziehung zur röntgenographisch bestimmten prozentuellen Kristallinität steht. Ebenso besteht eine lineare Beziehung der Dichte zur Absorption in gewissen Absorptionsbanden im Infrarotspektrum von isotaktischem Polypropylen. Die Infrarotdaten erlauben eine Bestimmung der Dichte des amorphen Polymeren, welche in guter Übereinstimmung mit Literaturangaben und mit einem durch Extrapolation der Röntgendaten auf die Kristallinität Null bestimmten Wert ist. Es wird gefunden, dass eine ungefähre, angenähert lineare Beziehung zwischen Kristallinität (aus der Dichte) des nichtextrahierten Polypropylens und dem Prozentgehalt an unlöslichem Rückstand nach der Extraktion mit siedendem n-Heptan, oder nach schrittweiser Extraktion mit anderen Lösungsmitteln und Heptan, besteht. In allen Fällen übersteigt die Menge des Rückstandes den kristallinen Anteil. Die Beziehung zwischen Kristallinität and Unlöslichkeit wird vom Molekulargewicht (nach der Viskositätszahl geschätzt) beeinfluss. Eine Zunahme der Kristallinität bei konstanter Viskositätszahl entspricht einer Zunahme der Unlöslichkeit; bei konstanter Kristallinität entspricht eine grössere Viskositätszahl einer grösseren Unlöslichkeit. In bezug auf seine Dichte kann das unextrahierte Polymer nicht einfach als eine Mischung zweier gut definierter Komponenten betrachtet werden, da die Dichte des unlöslichen Rückstandes mit der Dichte des ursprünglichen Gesamtpolymeren zunimmt.