The Determination of the Relative Isotactic Content of Polypropylene by Extraction

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INTRODUCTION

The crystallinity or degree of order of polypropylene depends not only upon the absence of significant amounts of chain branching, but also upon the degree of steric regularity (isotacticity) of the asymmetric carbon atoms in the polymer chain. As the mechanical properties of isotactic polypropylene are markedly different from those of less ordered polypropylenes, the amount of isotactic material present in a sample must be known if consistent results are to be obtained in studies of mechanical properties.[1,2] Moreover, with the increasing commercial use of polypropylene, it becomes necessary to establish a standard method of determining the isotactic character of various polymer grades.

Several methods have been used to estimate the isotactic content of polypropylene, such as x-ray studies,[3] density determinations,[4] infrared spectroscopy,[4-6] and solvent extraction procedures.[7]

None of these has as yet been universally accepted as an absolute standard, and agreement between two different methods is not always too good. The density and x-ray methods depend upon the completeness of crystallization of the isotactic material in the sample, and as a result the values are difficult to reproduce, even with careful annealing.

One of the most commonly used estimates of steric regularity is the amount of material unextracted by hot heptane. This has been referred to as an isotacticity index.[1] Natta and his co-workers[2] studied the solubility of polypropylenes in various solvents. They found that diethyl ether removed lower molecular weight polymer which showed no crystallinity by the x-ray method. Subsequent extraction with *n*-pentane removed material having about the same intrinsic viscosity as the ether-soluble material, but which was about 30% crystalline. In going from C_5 to C_8 saturated hydrocarbon solvents, they found progressive increases in both the x-ray crystallinities and intrinsic viscosities. The normal octane-extractable material was nearly as crystalline as the residue, but its intrinsic viscosity was about half that of the residue. They reasoned that these intermediate fractions were essentially block polymers of the *d* and *l* forms, caused by occasional inversion of configuration as the chain grew, giving chain configurations such as: *ddddlllllllddddddllllll*, etc. They term such polymers "stereoblock." Thus, the ether-soluble fractions are generally considered atactic and the heptane-soluble to be stereoblock polymer.

Natta and his co-workers describe[7] a procedure involving use of a relatively large amount of polymer and extraction for up to 40 hr. with acetone, then repeating with ether and heptane at the boiling point of the solvent under a nitrogen atmosphere to avoid the possibility of oxidation. These same authors also reported that one fraction tended to solubilize the less soluble material. Most authors, however, give only general descriptions of the extraction procedure used. In ordinary Soxhlet-type extractions, both the ether- and heptane-extractable values may vary as much as 5% for polypropylenes of medium isotacticity.

The studies described in this paper were undertaken to find out whether reproducible, but not necessarily absolute, values of isotacticity could be obtained in a relatively short time, whether oxidation of the polymer during extraction would seriously affect the results, and to examine other variables affecting extraction. As acetone extraction is pertinent only in the case of very crude polymer, it was not studied.

EXPERIMENTAL

Experience with the extraction of polypropylenes shows that there are several factors involved which can lead to variable results if not taken into ac-
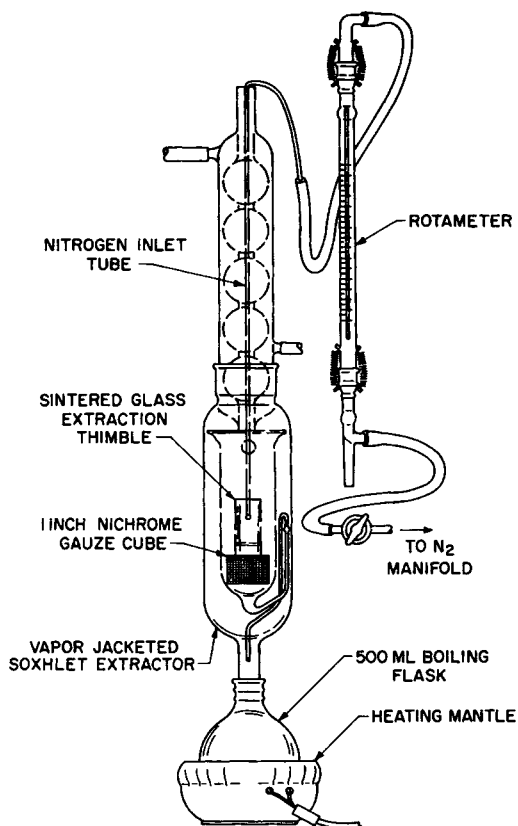
Fig. 1. Extraction apparatus.

count. In using the conventional Soxhlet extractors, the temperature of the extraction chamber is quite critical. The use of cellulose extraction thimbles required careful drying and weighing procedures due to pickup of moisture by the thimble. The weighing of the extracted material after evaporation of the solvent was a troublesome procedure and proved difficult to reproduce.

The extraction temperature problem was largely overcome in the present work by the use of vapor-jacketed Soxhlet extractors, thus maintaining the temperature at that of the boiling solvent. The use of sintered glass extraction thimbles avoided the troubles caused by the cellulose thimbles. It was found advantageous to support the glass thimbles on a 1-in. cube of nichrome gauze in the extraction chamber, thus allowing better drainage between cycles of the extractor. The vapor-jacketed Soxhlet extractors used were the large size made by the Emil Greiner Co., New York, and the glass extraction thimbles were 35 × 90 mm. with a coarse porosity fritted disk. Tubes for the introduction of nitrogen were inserted loosely down through the condenser of the Soxhlet to about 2 in. above the

sample in the thimble. To reduce heat loss, aluminum foil was wrapped around the extraction chamber. The flow of nitrogen was controlled separately for each extractor from a manifold using glass laboratory rotameters to measure the flow rates. The apparatus is illustrated in Figure 1.

The "standard" extraction procedure was as follows: Duplicate samples weighing 2.0000 to 2.2000 g. were placed in tared thimbles. These were placed in the extractors on the nichrome wire gauze cubes and the nitrogen inlet tubes inserted. After the nitrogen flow in each extractor was adjusted to about 10 cc./min., the samples were extracted with 300 ml. of diethyl ether for 6 hr. The units were heated so as to give a cycling time of 12 min. The samples were then removed and dried overnight in a hot plate oven under a stream of nitrogen flowing at the rate of 100 cc./min. at 60°C. A sketch of this hot plate oven is found in Figure 2. This oven merely sits on top of an adjustable hot plate. After drying, the weight losses of the thimbles were determined. The samples were again placed in the extractors and extracted with 300 ml. of n-heptane (b.p. 98–99°C.) for 6 hr. under a flow of 100 cc./min. of nitrogen. The samples were dried and weighed as before.

The polypropylenes studied are listed in Table I. None of these polymers showed evidence of degradation in their infrared spectra. Samples A, G, and E were unstabilized polypropylenes samples in powder form. H, I, and J were different batches
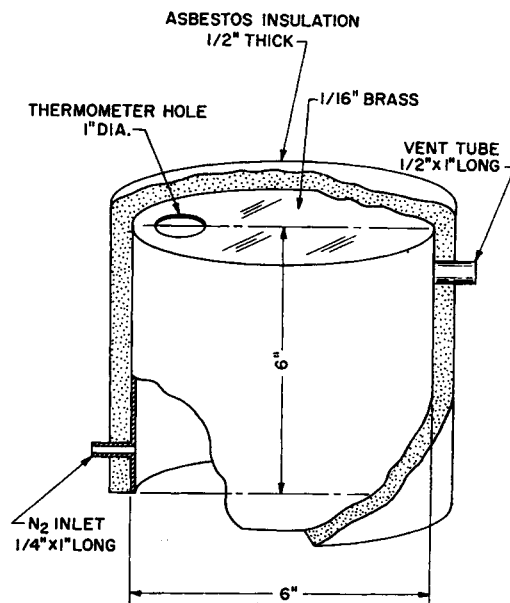

Fig. 2. Hot plate oven.

of the same polymer as G which were stabilized and in the form of commercial pellets. The remaining samples were commercial pellets of different grades and manufacturers containing stabilizers. For preliminary studies to set up a reproducible method samples A and E were used.

TABLE I
Polypropylene Samples

Polymer	Melt index at 230°C.	Remarks
A	Degrades	Experimental sample, no stabilizer
B	1.07	
C	2.08	
D	3.29	
E	4.5[a]	Base flake, no stabilizer
F	0.164	High M. W. resin
G	2.11	Base flake, no stabilizer
H	3.09	
I	1.15	
J	1.71	
K	0.18	Moderately isotactic
L	0.16	Highly isotactic

[a] At 190°C.

DISCUSSION AND RESULTS

Effect of Nitrogen and Cycling Time

The results of the initial extractions are given in Table II. Where repeated extractions with a solvent were carried out, the values given are the cumulative total percentages extracted with ether or heptane. The chief considerations here were the use of nitrogen and the time required for extraction to essentially constant values. It was found that the fastest cycling time of the Soxhlets without flooding or splashing on the sample was about 12 min. The samples were extracted for 6-hr. periods at this rate. In the first two runs the nitrogen flow was not measured, and the cycling time was long—about 20 min. It will be noticed that repeated 6-hr. extractions did not give constant values in these runs.

The effect of nitrogen is better illustrated in the next five extractions in which the metered nitrogen flow rates were varied at 0, 10, and 100 cc./min. For these, the cycling rate of extractor was once every 12 min. The second 6-hr. extraction with heptane in Run 3 at 100 cc./min. of nitrogen flow removed only about a 0.5% more material. The subsequent extraction without nitrogen removed an additional 1%. In Run 6, at a flow of nitrogen of 100 cc./min., the second 6-hr. extraction removed

essentially no more material. No nitrogen was used in Run 5, and the material extracted by heptane (22.1%) was noticeably higher than the extraction values of 20.1 to 20.6% obtained with nitrogen. Moreover, the residue was seen to gain weight due to pickup of atmospheric moisture, which indicated oxidative degradation. The results of Run 7 indicate that reducing the nitrogen flow rate to 10 cc./min. also gives higher results on continued extraction with heptane.

The ether-extractable values appear to be quite reproducible under the conditions of extraction, the range being 1.7–1.9% for all the ether extractions of polymer B. The removal of ether-soluble material appeared to be essentially complete in 6 hr. The absence of nitrogen in the ether extraction did not change either the ether or heptane values (Runs 8 and 9). A slow flow of nitrogen (10 cc./min.) was used in subsequent ether extractions to avoid atmospheric moisture condensing in the apparatus on humid days.

Reproducibility

The last four runs listed in Table II are essentially checks upon the method as described in the experimental part. The variation in the amount of ether-soluble material was 0.2% and that of the heptane-soluble was 1.0%. Without the use of the vapor-jacketed extraction chambers and nitrogen, the variation in ether and heptane-soluble fractions would normally be about 0.5 and 3.0%, respectively, for material of this type.

Extraction of Various Polypropylenes

Table III lists the results obtained on extracting various polypropylene samples in duplicate. The first three, A, G, and E, were all unstabilized and finely divided. The residues from A were somewhat higher than those obtained with an unknown flow of nitrogen. As this was the most finely divided of all the samples, it would presumably be very susceptible to air oxidation at the boiling point of heptane (98°C.). The values of E are in agreement with those obtained earlier. The 94.4% residue of G agrees well with 94.3% obtained in a large-scale extraction of this polymer with heptane to constant weight under an excess of nitrogen.

The remaining samples were in the form of pellets. Various methods to pulverize the samples, such as grinding in a pelletizer, pounding at Dry Ice temperature, and cold milling, were tried, but none were successful. Solution and reprecipitation

TABLE II
Effect of N_2 and Duration of Extractions

Polymer	Run No.	Solvent	1st 6 hr.		2nd 6 hr.		3rd 6 hr.		Final % insol.
			N_2 flow, cc./min.	% Sol.	N_2 flow, cc./min.	% Sol.	N_2 flow, cc./min.	% Sol.	
A	1	Et$_2$O	a	3.2	a	3.9			
		Heptane	a	15.1	a	15.5	a	16.2	79.9
A	2	Et$_2$O	a	3.3	a	3.7			
		Heptane	a	14.0	a	14.6	a	15.2	81.1
E	3	Et$_2$O	100	1.9					
		Heptane	100	20.1	100	20.6	0	21.6	76.5
E	4	Et$_2$O	100	1.7					
		Heptane	100	20.6	0	22.6	0	23.7	74.6
E	5	Et$_2$O	100	1.7					
		Heptane	0	22.1[b]					76.2
E	6	Et$_2$O	100	1.7					
		Heptane	100	20.3	100	20.4			77.9
E	7	Et$_2$O	100	1.8					
		Heptane	10	22.8	10	23.5			74.7
E	8	Et$_2$O	0	1.8					
		Heptane	100	20.1					78.1
E	9	Et$_2$O	0	1.7					
		Heptane	100	20.6					77.7
E	10	Et$_2$O	10	1.9					
		Heptane	100	28.8					77.3
E	11	Et$_2$O	100	1.8					
		Heptane	100	19.6					78.6

[a] Slow flow of N_2, not metered.

[b] This sample could be seen to pick up atmospheric moisture.

TABLE III
Extraction of Various Polypropylenes.   "Standard" Procedure

Sample	% Et$_2$O-soluble	% Heptane soluble	% residue	% Isotactic (infrared data)[a]	
				Et$_2$O-extracted	Heptane-extracted
A	3.3	10.8			
	3.3	11.7	85.4	0[b]	22
G	1.4	4.3			
	1.4	4.1	94.4	0[b]	38
E	1.7	21.0			
	1.7	20.5	77.5	0[b]	28
B	0.4	2.4			
	0.4	2.1	97.3	—	—
C	0.4	5.0			
	0.4	4.5	94.8	—	—
D	0.4	6.2			
	0.4	5.5	93.7	—	27
F	1.4	2.1			
	1.4	2.2	96.4	—	—
H	1.4	1.7			
	1.5	1.7	96.8	—	29
I	1.8	1.8			
	1.8	2.1	96.2	—	33
J	1.9	2.5			
	1.9	2.6	95.5	—	—
K	1.1	5.7			
	1.1	6.1	93.0	—	22
L	0.7	1.7			
	0.6	1.7	97.6	—	—

[a] Obtained by J. P. Luongo.

[b] Within the accuracy of the method.

procedures were considered, but here one could not be sure that fractionation of the sample would not occur to varying degrees. The pellets were finally milled as thin as possible (avg. 2–5 mil) on a warm mill.

The agreement for the ether-soluble fractions of duplicate samples is quite good. In all but the first three, antioxidants and stabilizers were present and were removed in the ether extractions. No isotactic material was detected by infrared spectroscopy in the ether extracts of these stabilized samples. However, the bands due to the stabilizers would mask bands caused by the presence of a small amount of isotactic polymer. The infrared spectra also showed no evidence of stabilizers in the heptane-soluble fractions if the sample had been previously extracted with ether. In discussing the ether-soluble fractions of commercial samples it must be kept in mind that part of this material is the stabilizing system.

The 2% difference in the heptane-soluble contents of the commercial pellets of H, I, J pellets and the powdered polymer G is noteworthy. The difference in particle size seems to be responsible; however, further extraction with heptane did not remove any significant amount of material. The flattened pellets apparently still do not have sufficient surface area for efficient extraction, although results in the pellets appear consistent within themselves. It is possible, of course, that in the pelletizing process the crystallization of the polymer may have become more complete and the amount of extractable material thereby lowered. The ether-soluble data for samples also show this effect if one takes into account the extraction of the stabilizers. For reliable testing, the physical form of the samples must be carefully specified.

Extraction by Heptane Only

Extractions with heptane alone without the use of nitrogen have given erratic results in ordinary Soxhlet extractors. However, when the three samples without additives were extracted in a nitrogen atmosphere with only heptane by the procedure described above, the values for residues obtained were as follows: polymer A, 84.5%, 84.9%; polymer G, 94.4%, 94.3%; polymer E, 76.7%, 77.0%. These values compare well with the average values of 85.4, 94.4, and 77.6%, respectively, found by use of the ether–heptane extraction system. Because the use of a single heptane extraction would cut the time required in half, this would be advantageous providing that only the total insoluble

residue of a sample is required and the amount of ether-soluble material is not of interest.

Infrared Examination of Soluble Fractions

Infrared studies of the extracts were carried out by J. P. Luongo of these laboratories.

The heptane-soluble portions of the various polypropylenes contained about 22–38% isotactic polymer as measured by infrared. The infrared spectra of these fractions showed no features which could not be accounted for by the isotactic and atactic forms. The spectra were typical of mechanically mixed atactic and isotactic polypropylenes. As a result, the existence of the stereoblock form could not be confirmed by infrared means. The work of Natta,[2] however, does show that the heptane-soluble polypropylenes have mechanical properties distinctly different from those of the atactic and isotactic materials, particularly in regard to their elastic nature. This is not true, according to Natta, for mere isotactic–atactic mixtures. It appears advantageous, therefore, to know the relative amount of the "stereoblock" material as well as that of atactic and isotactic polymer. Percentages of the isotactic polymer, as determined by the infrared method, are listed in Table III. The standard for "100% isotactic" polymer was the residue of polymer G after extraction to constant weight with heptane, so in reality all our values of isotacticity by infrared are relative to this.

Because stabilizers were present in the others, the only ether-soluble fractions which could be suitably analyzed by infrared means were those of the three base flake samples, A, E, and G. No isotactic material could be detected in any of these three base flake extracts, even in the case of the low molecular weight (based on melt index) polymer E. This would seem to confirm Natta's results that ether is incapable of extracting material which possesses any significant degree of order. On the other hand, since molecular weight studies of the various fractions were deferred to a later time, one cannot be certain that all the completely atactic material of the higher molecular weight was extracted from the sample by the ether. Until these structural problems are further clarified, it appears safest to regard the heptane-soluble fractions as ones possessing ranges of order intermediate between those of isotactic and atactic polypropylene. This would account for the lack of uniqueness in the infrared spectra of the heptane-soluble material.

It is also apparent from Table III that the isotactic values for the heptane-soluble fractions are

not related to the total percentage of heptane-soluble material present in the original polymer. The large heptane-soluble fraction of E and the small heptane-soluble fraction of the highly isotactic H have about the same isotactic content as determined by infrared.

CONCLUSIONS

A measure of the isotactic content of polypropylene may be obtained by successive extractions with diethyl ether and n-heptane or with n-heptane alone under controlled conditions. Although the values obtained cannot be regarded as absolute, they are reasonably reproducible and could serve to characterize polypropylenes. It is necessary to extract under nitrogen at the boiling point of n-heptane due to the high rate of oxidation of unstabilized polypropylene at elevated temperatures. The chief problem which remains is the grinding of commercial pellets to a small enough size for satisfactory extraction.

Although the extraction method takes a longer time than the infrared procedure and also cannot be considered to give an exact value of the isotactic content of a polypropylene, it may be useful wherever the presence of stabilizers and other additives may make the use of infrared studies difficult. Moreover, the individual soluble fractions can be isolated and their effects on mechanical properties studied further.

Infrared studies confirmed that the material soluble in ether does not contain any detectable degree of order and hence can be considered atactic. The heptane-soluble fractions, however, do contain a range of order corresponding to 20–40% isotactic polymer.

References

1. Ranalli, F., and G. Crespi, *Modern Plastics Encyclopedia*, Modern Plastics, New York, 1960, pp. 142–145.

2. Natta, G., G. Mazzanti, G. Crespi, and G. Moraglio, *Chim. e ind. (Milan)*, **39**, 275 (1957).

3. Natta, G., P. Corradini, and M. Cesari, *Atti accad. nazl. Lincei, Rend Classe sci. fis. mat. e nat.*, **22**, 11 (1957).

4. Quynn, R. G., J. L. Riley, D. A. Young, and H. D. Noether, *J. Appl. Polymer Sci.*, **2**, 166 (1959).

5. Heinen, W., *J. Polymer Sci.*, **38**, 545 (1959).

6. Luongo, J. P., *J. Appl. Polymer Sci.*, **3**, 302 (1960).

7. Natta, G., P. Pino, and G. Mazzanti, *Gazz. chim. ital.*, **87**, 528 (1957).

Synopsis

Attention is called to the variables effecting the extraction of polypropylene. Under controlled conditions, the extraction of polypropylene with first diethyl ether and then n-heptane will give reproducible results. It is necessary to extract with heptane in an atmosphere of nitrogen. The values obtained by the extraction procedure described are regarded as relative measures of the amounts of isotactic, stereoblock and atactic material present in a sample. Extraction with n-heptane alone by this procedure also gives the same value of relative isotacticity. Infrared studies showed that the ether soluble fractions were essentially atactic, while the n-heptane-soluble or stereoblock material possessed a degree of order corresponding to 20–40% isotactic polypropylene.

Résumé

On attire l'attention sur les variables influençant l'extraction du polypropylène. Dans des conditions définies, l'extraction du polypropylène, d'abord par l'éther diéthylique, ensuite par le n-heptane donne des résultats reproductibles. L'extraction par l'heptane doit nécessairement être faite sous atmosphère d'azote. On considère que les valeurs obtenues par les processus d'extraction décrits, sont des mesures relatives des quantités de produits isotactiques, stéréoblocs et atactiques présentes dans l'échantillon. L'extraction unique par le n-heptane, suivant ce processus nous donne également les mêmes valeurs de l'isotacticité relative. Des études infra-rouges nous ont montré que les fractions solubles dans l'éther diéthylique sont essentiellement atactiques, tandis que les produits solubles dans le n-heptane ou stéréoblocs possèdent une disposition interne correspondant à 20 à 40% de polypropylène isotactique.

Zusammenfassung

Es wird die Aufmerksamkeit auf die Variablen gelenkt, welche die Extraktion von Polypropylen beeinflussen. Unter kontrollierten Bedingungen liefert die Extraktion von Polypropylen, zuerst mit Diäthyläther und dann n-Heptan, reproduzierbare Ergebnisse. Die Extraktion mit Heptan muss in einer Stickstoffatmosphäre erfolgen. Die durch den beschriebenen Extraktionsvorgang erhaltenen Werte werden als relatives Mass für die in der Probe vorhandenen Mengen an isotaktischem, Stereoblock- und ataktischem Material betrachtet. Die Extraktion mit n-Heptan allein liefert nach diesem Verfahren den gleichen Wert für die relative Isotaktizität. Infrarotuntersuchung zeigte, dass die ätherlöslichen Fraktionen im wesentlichen ataktisch waren, während das n-heptanlösliche oder Stereoblock-Material einen Ordnungsgrad entsprechend 20 bis 40% isotaktisches Polypropylen besass.