Factors Affecting the Heptane Solubility of Polypropylene Polymers and Yarns

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Synopsis

The heptane solubility of polypropylene yarns prepared under a variety of experimental conditions from several molecular weight ranges of polymers has been examined. The heptane solubilities of the yarns have been found to vary over a wide range, depending upon the conditions of extrusion during fiber formation and the subsequent degree of orientation of the fibers. The solubility of the yarns increases with higher spinning temperatures presumably as a function of the formation of low molecular weight soluble fractions formed as a result of thermal degradation. A reduction in the solubility occurs as the yarns are oriented either during the winding operation or by subsequent drawing. The reduced solubility has been explained on the basis of increased molecular alignment thereby promoting increased crystallinity as well as the possible entrapment of normally soluble atactic polymer. The fact that the polymer solubility can be decreased by bringing the polymer to a higher state of crystallinity has been shown by annealing studies. The solubilities of the original polymers, therefore, exhibit little correlation with the yarns produced from them. The solubilities of the annealed polymers, however, more closely approach the values obtained for the highly oriented yarns.

INTRODUCTION

The solubility of polypropylene polymers in boiling heptane has been widely used as an index of the isotactic content of the polymers.[1-4] Little work, if any, however, has been devoted to the elucidation of the heptane solubility characteristics of fibers and yarns produced from polymers (the literature describes methods and results on polypropylene polymers prior to being melt-spun). Our research was undertaken to determine whether any correlation existed between the heptane solubility of these polypropylene polymers and the melt-spun fibers and yarns produced from them in order to obtain a better understanding of the effect of polymer isotactic content on yarn behavior. During the study it was found that there are several other factors besides isotactic content which can influence the solubility of the polymers and yarns. The other factors are those which are normally encountered during the extrusion and orientation steps involved in the fabrication of fibers.

Specifically, the variation of heptane solubility of various polypropylene polymers and yarns has been correlated with average molecular weight,

TABLE I
Polypropylene Polymers Studied

Polymer	Inherent viscosity η_i, dl./g.	Molecular weight $\bar{M}_w \times 10^{-5a}$	Melt index at 230°C., g./10 min.[b]	Density, g./cc.[c]	Heptane insolubility, %	
					As received	Annealed[d]
A	2.88	3.90	1.18	0.902	95.1	97.7
B	2.66	3.51	1 65	0.901	89.5	95.8
C	2.07	2.55	7.10	0.902	94.2	96.1
D	2.03	2.48	5.28	0.902	93.0	95.3
E	1.68	1.95	8.40	0.902	90.6	97.3
F	1.78	2.12	10.92	0.902	89.2	96.4

[a] $[\eta] = 1 \times 10^{-4}\, \bar{M}_w^{0.80}$ where constants were derived by Chiang for a decalin solvent system.
[b] 0.0825 in. I.D. orifice, 2160 g. load, ASTM D569-59.
[c] At 23°C., ASTM 1505-60-T.
[d] At 120°C., 4 hr. in vacuum oven.

orientation, and crystallinity. It is a characteristic of polypropylene that extrusion at elevated temperature is accompanied by a reduction and a redistribution of the molecular weight. The extent of these changes is a function of the extrusion temperature and residence time. The rate at which the extrudate is cooled and the tensions imposed on the extruded filaments are all reflected in the degree of orientation of the extrudate, in the degree of crystallinity, and in the crystalline structure of the yarn. Subsequent orientation of the filaments results in further structural changes which take place without further modification of the molecular weight. The changes in molecular weight, the birefringence of the yarns, which is commonly used to estimate the increased alignment due to orientation, and the densities of the yarns as an indication of crystallinity have all been related to heptane solubility.

Heptane solubility has been considered to be an index of the crystallizable potentialities of a given polymer and various correlations have been shown between density, crystallinity, and isotacticity.[5,6] Many of the mechanical and physical properties of polymers have been correlated with the total fraction of crystalline material by various investigators. Nielsen[7] discusses the effect of isotacticity and crystallinity of semicrystalline polymers on shear modulus. Wijga,[8] in discussing factors governing crystallinity, gives the relationship between atactic polymer content (as percentage extractable) and yield strength. Kresser[9] has reported that the permeability of liquids such as toluene and carbon tetrachloride is less for polymers of higher crystallinity. In addition, it has also been reported that factors such as stiffness, hardness, temperature resistance, and strength are dependent upon crystallinity. In general, the accepted role of the isotactic content of polymers as related to the properties of fibers and yarns is that the yarns will also reflect those properties which are normally associated with high crystallinity, such as greater stiffness, improved elevated temperature behavior, resistance to creep, good recovery properties, high strength, etc. In contrast, the reverse effects are produced by lower isotactic polymers. The polypropylene polymers used in these studies were of various molecular weights and isotactic contents as determined on the polymer pellets as obtained from the polymer manufacturer.

EXPERIMENTAL

Materials

The polypropylene polymers considered in this study were obtained from Enjay Chemical Company, a division of Humble Oil and Refining Company. The polymers were selected from a group submitted to offer a wide range of heptane insolubilities and molecular weights and are listed in Table I. They represent a range of molecular weights, $\bar{M}_w$, from about 195,000 to 390,000 (or inherent viscosity of 1.68 to 2.88). The melt index varied from 1.2 to 11.0 g./10 min. through a 0.0825 in. I.D. orifice at 230°C.

with 2160 g. load.   Actually, the polymers can be grouped roughly into three categories according to dilute solution viscosity and melt viscosity as high molecular weight with inherent viscosity over 2.5, intermediate group with inherent viscosity from 1.9 to 2.10, and lower molecular weight with inherent viscosity under 1.90.   The heptane insolubilities varied from 89 to 95%.   A short investigation was also made on an additional polypropylene polymer having an "as received" heptane insolubility of 86.5%. However, because of limited amount of polymer, the spinning study in this case was limited.

The experimental yarns were melt-spun with the use of a conventional extruder with a metering pump feeding the spinnerets.   Comparative yarns were spun through a 50-hole 16 mil (400 μ) spinneret at a polymer throughput of 62 g./min. (8.2 lb./hr.) and were wound at 2260 ft./min. to give an undrawn yarn of 820 den.   The spinning temperature was varied to give yarns melt spun from approximately 275–330°C.   An additional series of yarns were produced from two polymers by varying the winding speed at three different spinning temperatures representing high, intermediate, and low settings.   The undrawn yarns were measured for inherent viscosity, heptane insolubility and birefringence prior to being drawn.

Yarns were drawn by use of conventional stretching equipment at 570 ft./min. over a heated plate maintained at 120 ± 2°C.   A series of drawn yarns were produced at draw ratios up to about 6:1 or to the maximum possible for the particular spinning conditions.   Yarn birefringence and heptane insolubility were determined on these drawn yarn samples.

Test Methods

Dilute solution viscosities were determined on the original polymer and melt spun yarns in accordance with the ASTM designation 1601–58T. The results, expressed in terms of inherent viscosity, were determined on 0.1% polymer concentration in decalin at 135°C.   The intrinsic viscosity was estimated and molecular weight $\bar{M}_w$ calculated by using the conversion equation reported by Chiang.[10]

Melt flow rates were determined on the original polymer by extrusion plastometer described in ASTM Designation D1238-57T to give a melt index value at 230°C. using the standard 0.0825 in. I. D. orifice and load of 2160 g. (approx. pressure 43.25 psi).

Birefringence on the undrawn and drawn filaments was determined by using a Berek compensator in conjunction with a polarizing microscope. Samples were mounted in Permount and extreme care was exercised so that undrawn yarn was not stretched.   By obtaining the retardation value and the fiber thickness at point of retardation measurement, the birefringence could be calculated.   The general technique follows established procedures.[11]

Densities on original polymer pellets and spun yarns were obtained by the density-gradient technique, ASTM Designation D1505–60T, ethylene glycol–isopropanol being used as the liquids.

The heptane insolubility was determined on 1.5 g. samples by a 3-hr. extraction with boiling heptane. Under the conditions of the test, increasing the time of extraction up to 21 hr. did not significantly change the level of results. The original polymer samples were extracted in finely divided powder form by grinding in a Wiley mill. Yarn samples were treated "as received" except where finish was present. In those cases the finish was removed prior to extraction. The samples were retained in medium porosity alundum extraction thimbles and extracted in vapor-jacketed Soxhlet extraction chamber.

Ground polymer samples were annealed by heating at 120°C. for 4 hr. under vacuum and cooling. Viscosity measurements made on the original and heat-treated samples indicated that thermal degradation in absence of air was negligible. Time–temperature curves were obtained to indicate that annealing for 4 hr. at 120°C. was sufficient to reach a constant heptane insolubility and density.[12,13]

RESULTS AND DISCUSSION

Polymer Properties

The melt flow properties of the polypropylene polymers are given in Table I, together with the density of the polymers, the solubility in boiling heptane, and the polymer chip inherent viscosity. In addition, the boiling heptane solubility of the annealed polymers is also shown. The melt flow properties of the polymers reflect the differences in molecular weight and indicate that extrusion conditions will have to be altered for each polymer group.

Extrusion

The average molecular weight of the polypropylene polymers decreases during the conversion of polymer chip into fiber during the melt spinning operation if the melt temperature is sufficiently high. The amount of molecular weight degradation which occurs is a function of the spinning temperature and throughput. The data shown in Figure 1 indicate that the level of the yarn molecular weight ($\bar{M}_w$) versus extrusion temperature curve depends upon the original molecular weight of the polymer since all the polymers under discussion were extruded at the same throughput rate.

Heptane solubility is also dependent upon the extent of molecular weight degradation which has occurred as a function of the spinning temperature. The heptane solubility increases as the spinning temperature is increased. This is shown in Tables II, III, IV, and V for four polymers representing the various molecular weight ranges under consideration. Tables III and IV show that the factor of orientation of yarns extruded at constant temperature (i.e., constant molecular weight) has an effect on the heptane solubility. As the winding speed is increased, thereby increasing the orientation due to higher drawdown tensions, the heptane solubility is decreased.
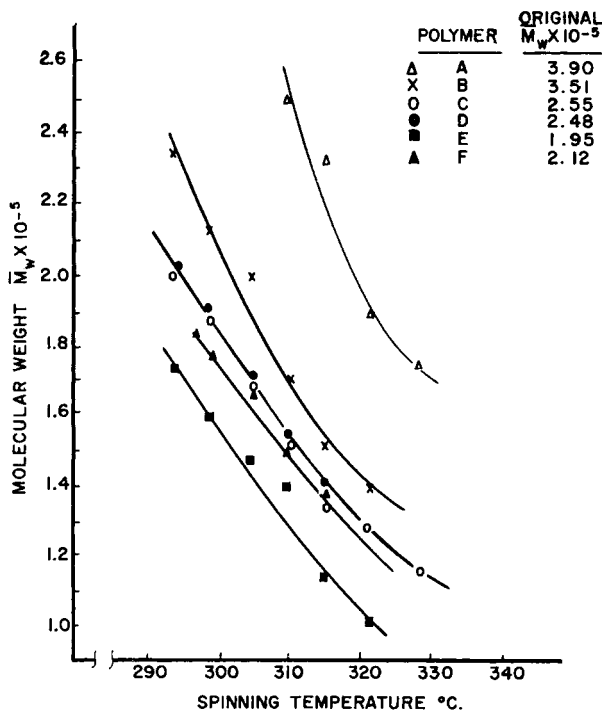
Fig. 1. Variation in molecular weight of polypropylene yarn with spinning temperature. A study involving six polypropylene polymers spun at a throughput of 62 g./min.

The change in density of the yarns as a function of spinning temperature under cooling conditions of constant air temperature and velocity are shown in Table V.   Density, of course, has been related to the degree of crystallinity.[6,14]   X-ray data characterizing the undrawn yarns from polymers extruded at a series of temperatures have shown that both the crystalline structure and the degree of crystallinity are different, depending upon the melting temperature of the polymer.   Yarns extruded at the lower spinning temperatures have shown patterns of high crystallinity of the monoclinic structure, and the level of crystallinity has been found to increase as the

TABLE II

Effect of Spinning Temperature and Yarn Inherent Viscosity on Yarn Heptane Insolubility (Polymer B, η_{chip} = 2.66)

Spin temperature, °C.	Yarn inherent viscosity, dl./g.	Heptane insoluble, %
294	1.95	96.9
299	1.78	93.0
310	1.43	89.4
315	1.36	88.6
321	1.25	87.9

TABLE III

Effect of Spinning Temperature, Winding Speed, Yarn Inherent Viscosity, and
Birefringence on Yarn Heptane Insolubility (Polymer A, η_{chip} = 2.88)

Spin temperature, °C.	Yarn inherent viscosity, dl./g.	Winding speed, ft./min.	Birefringence	Heptane insoluble, %
299	2.49	1000	0.0164	98.5
		2260	0.0188	97.8
		3500	0.0194	97.2
315	1.82	1000	0.0074	89.2
		2260	0.0157	90.6
		3500	0.0208	92.2
332	1.29	1000	0.0018	83.4
		2260	0.0068	84.3
		3500	0.0133	86.9

TABLE IV

Effect of Spinning Temperature, Winding Speed, Yarn Inherent Viscosity, and
Birefringence on Yarn Heptane Insolubility (Polymer D, η_{chip} = 2.03)

Spin temperature, °C.	Yarn inherent viscosity, dl./g.	Winding speed, ft./min.	Birefringence	Heptane insoluble, %
294	1.77	1000	0.0069	92.6
		2260	0.0145	96.2
		3500	C.0159	96.9
305	1.55	1000	0.0034	88.4
		2260	0.0098	89.9
		3500	0.0160	94.6
315	1.31	1000	0.0017	86.3
		2260	0.0079	89.1
		3500	0.0105	89.2

TABLE V

Effect of Spinning Temperature, Yarn Inherent Viscosity, and Density on Yarn Heptane
Insolubility (Polymer F, η_{chip} = 1.78)

Spin temperature, °C.	Yarn inherent viscosity, dl./g.	Density, g./cc.	Heptane insoluble, %
277	1.74	0.902	97.1
288	1.73	0.901	96.8
299	1.56	0.900	94.3
305	1.48	0.894	91.4
310	1.38	0.889	86.3
315	1.26	0.887	86.7
321	1.19	0.886	85.1

degree of orientation has been increased, such as by higher winding speeds. This is in contrast to yarns extruded at the higher spinning temperatures which have shown patterns indicating the paracrystalline structure. These differences in the degree of crystallinity are represented by the high and low density yarns of Table V, respectively.

Stretching

As the undrawn yarns are oriented, the birefringence is shown to increase, and the heptane solubility is shown to decrease. The decrease in solubility of the drawn filaments as compared to the undrawn filaments is apparently a function of the amount of orientation produced by drawing of the yarns as shown in Figures 2 and 3 for polymers D and F of Table I. However, it is apparent that when the initial insolubility of the "as spun" fiber is high, e.g., 97%, the reduction in solubility is slight or not readily apparent.

As the birefringence is increased by drawing the yarns, the heptane solubility decreases, as shown in Figures 4 and 5 for polymers D and F. As was
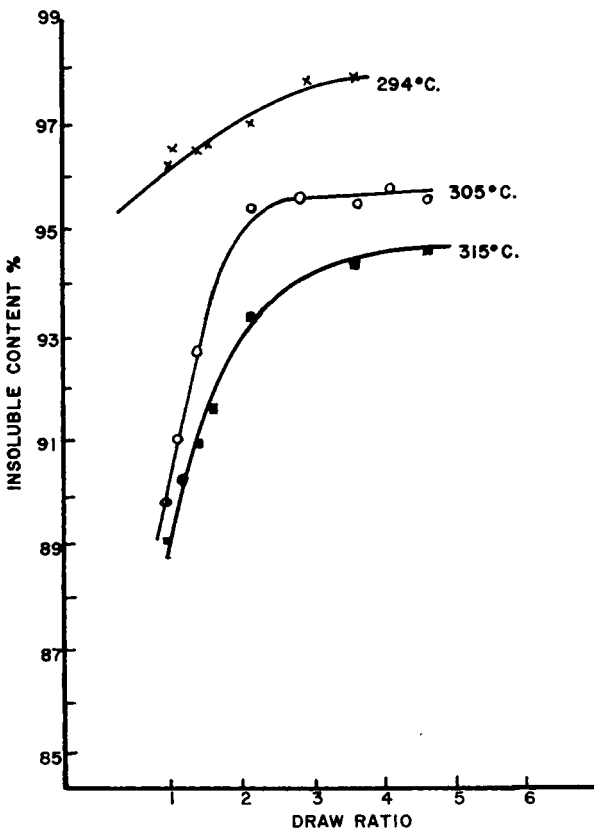

Fig. 2. Effect of draw ratio on the heptane-insoluble content of drawn polypropylene yarn. Samples of polypropylene polymer D spun at three spinning temperatures.
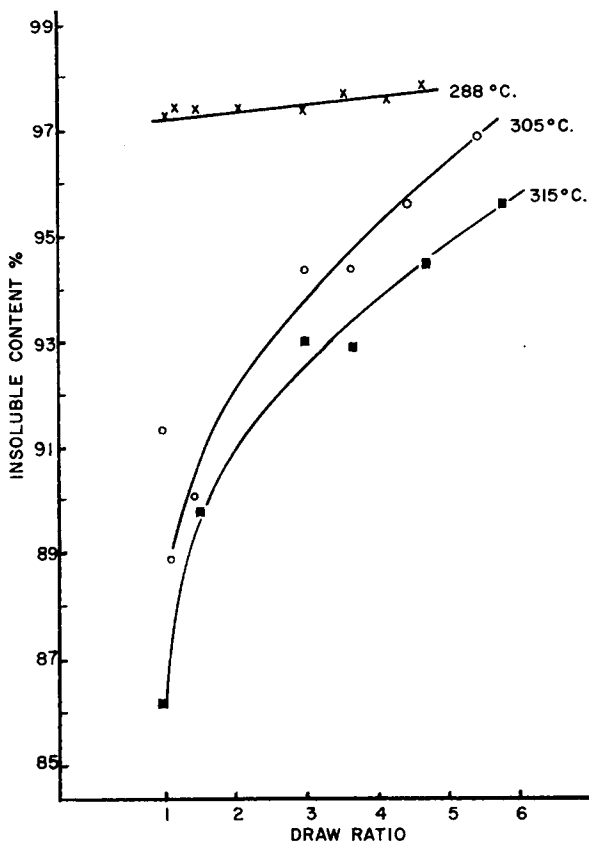
Fig. 3. Effect of draw ratio on the heptane-insoluble content of drawn polypropylene yarn. Samples of polypropylene polymer F spun at three spinning temperatures.

noted in spinning, the higher insolubilities occur with higher yarn molecular weights from a given polymer. Considerably greater orientation is required for yarns from a given polymer produced at a higher spinning temperature if they are to have the same insolubility as yarn produced at a lower spinning temperature. Presumably this will never be achieved for the polymer shown in Figure 2, for example, since the curves describing the solubility of the yarns spun at high temperatures appear to be leveling off.

It becomes apparent from the data that heptane insolubility as applied in this study is not only dependent upon the isotactic content but, in addition, is a measure of the degree of crystallinity and molecular alignment induced by processing conditions.

The extractability will vary according to such factors as soluble low molecular weight isotactic material, entrapment of normally soluble atactic material by crystalline polymer rendering it insoluble, and increased insolubility of the polymer when in the crystalline state. The literature has
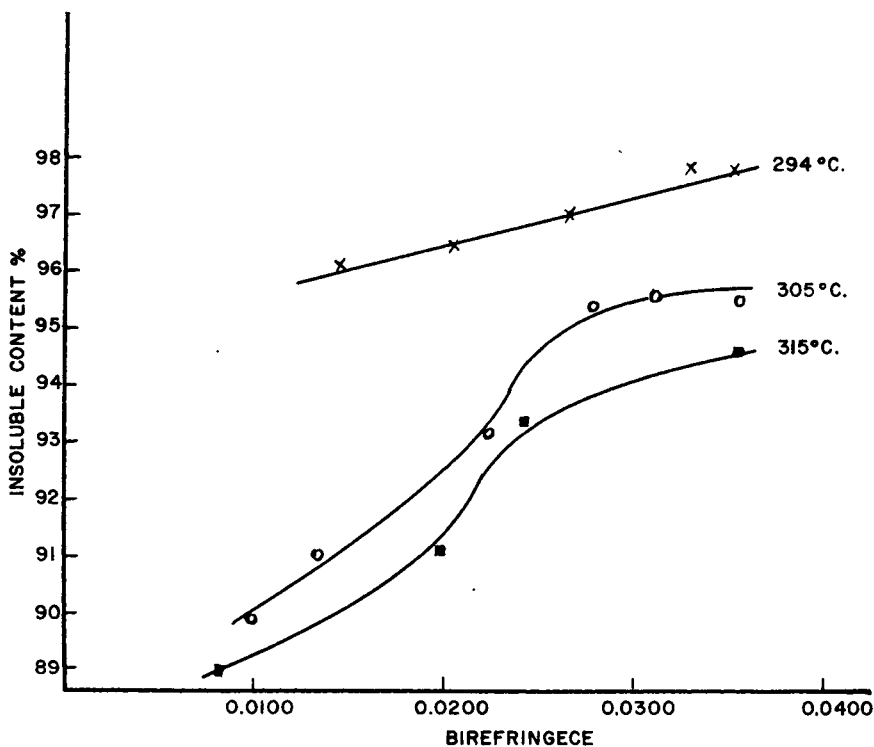
Fig. 4. Variation in heptane-insoluble content with yarn birefringence. Samples of polypropylene polymer D spun at three spinning temperatures.

suggested that the large atactic molecules may be trapped within a crystalline region or remain immobile in the solid phase.[6]

In order to investigate the effect of crystallinity on heptane solubility, "as received" polymer in finely divided state was annealed under vacuum. Annealing the polymer for 4 hr. at 120°C. caused a decrease in solubility in every case, as shown in Table I.   The final annealed heptane insolubility was lowest for the sample originally at 86.5%, the annealed insolubility being 91%.   There was no evidence of correlation between the "as received" and annealed insolubility.   A brief study of the influence of time and temperature on insolubility of resulting annealed polymers indicated that annealing takes place at very slow rate even at 90°C.   The rate at 115°C. is almost the same as at 120°C.   The work here is based on heating in a vacuum oven where the heat transfer is essentially by radiation.   The time, of course, becomes much shorter where polymer is in direct contact with metal surface or "wet-out" by immersion in nonreactive liquid, such as polyethylene glycol.[12,13]

The increase in heptane insolubility by annealing without changing the molecular weight is strong evidence that increased crystallinity decreases the solubility.   The decreased solubility in many instances may be greater
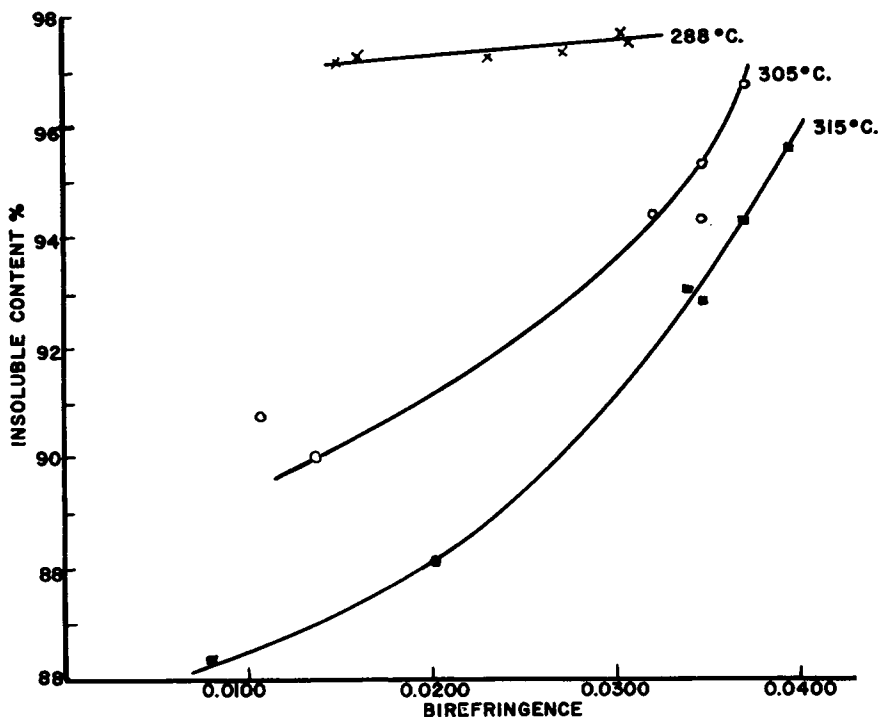
Fig. 5. Variation in heptane-insoluble content with yarn birefringence. Samples of polypropylene polymer F spun at three spinning temperatures.

in magnitude than can be attributed to isotactic molecules and, therefore, possibly includes the so-called "captive" atactic portion.

Based on the above considerations, it is therefore suggested that, in order to classify polypropylene pellet (chip) samples on the basis of heptane insolubility, the sample under consideration should be annealed prior to heptane extraction in order to present the polymer in its highest state of crystallinity. This procedure is comparable to the method that is used in the infrared and x-ray analysis of polymer samples. It is realized that the heptane insolubility of the annealed polymer pellet, while approaching the maximum value obtained on the drawn yarn, may be slightly less since drawing brings about a highly oriented molecular structure which might not be present in the annealed pellet.

SUMMARY AND CONCLUSIONS

Melt spinning causes a breakdown of the molecular weight of the polymer to a lower average value. It has been shown that the thermal degradation proceeds by a random breaking of the molecules and results in a change in the molecular weight distribution in which the tail of the distribution curve is broken down in the early stages of degradation with a resultant increase in polymer in the middle molecular weight range. Random degradation is

also accompanied by a breakdown of lower molecular weight species.[15] During the melting operation the length of time the polymer is in the melt, the temperature, and the shearing forces all have an effect on the structure of the molten polymer. This is of significance in the resultant structure of the solidified yarn. At low spinning temperatures, the thermal degradation is less. We would therefore expect a lesser amount of low molecular weight material compared to a higher temperature. Results have also indicated a higher degree of crystallinity presumably because of the presence of un-destroyed nuclei which act as crystallization centers on cooling. The higher birefringence values at the lower melt temperatures also indicate greater molecular alignment which apparently contributes to an increase in crys-tallinity. On the other hand, higher spinning temperatures degrade the polymer to a greater degree, thereby producing a larger amount of low molec-ular weight polymer chains capable of being extracted. The higher spin-ning temperature also results in polymer with a lower degree of crystallinity (presumably because of the destruction in the molten state of potential crystallization nuclei) which is more susceptible to extraction.

Differences in crystallinity and crystalline structure as a function of the rate of cooling from a given melt temperature and also resulting from ther-mal treatment have been reported.[16,17] Presumably, however, differences in solubility would not be expected to be evident as a function of the rate of cooling, since the slowly cooled yarn (higher crystallinity) would have prob-ably suffered a greater degree of molecular weight degradation which would tend to offset any decrease in solubility resulting from the increase in crystallinity.

The relationship between heptane insolubility and yarn inherent vis-cosity indicates a particularly strong trend in the reduction of heptane solubility with the higher molecular weight undrawn yarns produced from a given polymer. Probably in addition to the factors of reduced solubility of higher molecular weight polymer components is the factor of greater molecular alignment of the higher molecular weight yarns which not only enhances the possibility of additional crystallization but also might entrap otherwise soluble polymer.

Variation in heptane solubility during drawing is due to increased molec-ular alignment. Both insolubility and birefringence are correlated with draw ratio. Therefore, a highly insoluble fiber can be produced by drawing a low molecular weight material to high level of birefringence. An initially high heptane insoluble fiber limits drawing potentialities. The increase in birefringence starting with high insolubility is not reflected in solubility values. A maximum heptane insolubility appears to be approached at around 98%.

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Résumé

On a examiné la solubilité de fils de polypropylène dans l'heptane: les fils de polypropylène ont été préparés dans des conditions expérimentales variées à partir de polymères de poids moléculaires différents. Les solubilités des fils dans l'heptane varient sensiblement suivant les conditions d'extrusion pendant la formation de la fibre et du degré d'orientation des fibers. La solubilité des fils augmente avec de plus hautes températures de filature probablement par la formation de fractions solubles de bas poids moléculaires formés par dégradation thermique. Une diminution de la solubilité se présente quand les fils sont orientés soit durant l'extrusion soit par un étirage ultérieur. La diminution de la solubilité a été expliquée sur la base d'une augmentation d'alignement moléculaire lequel provoque une augmentation de la cristallinité ainsi qu'un piège possible d'un polymère atactique normalement soluble. Le fait que la solubilité du polymère peut être diminuée en portant le polymère à un plus haut état de cristallinité, a été montré par des études de recuit. Ainsi les solubilités des polymères originaux, montrent une faible corrélation avec les fils produits à partir de ces polymères. Les solubilités des polymères recuits cependant se rapprochent plus fort des valeurs obtenues pour les fils fortement orientés.

Zusammenfassung

Polypropylengarne wurden unter einer Reihe von Versuchsbedingungen aus Polymeren mit verschiedenem Molekulargewicht hergestellt und ihre Löslichkeit in Heptan untersucht. Die Heptanlöslichkeit der Garne zeigte je nach den Extrusionsbedingungen

während der Faserbildung und dem damit erzielten Orientierungsgrad der Faser einen
grossen Variationsbereich. Die Löslichkeit der Garne nimmt, wahrscheinlich wegen der
zunehmenden Bildung einer niedermolekularen, löslichen Fraktion durch thermischen
Abbau, mit höherer Spinntemperatur zu. Eine Herabsetzung der Löslichkeit tritt
durch Orientierung der Garne entweder beim Aufspulen oder bei späterer Reckung auf.
Die herabgesetzte Lösilchkeit wurde durch bessere Molekülausrichtung und dadurch
bewirkte höhere Kristallinität und möglicherweise auch Einschluss von normalerweise
löslichem ataktischen Polymeren erklärt. Eine Herabsetzung der Polymerlöslichkeit
durch Überführung des Polymeren in einen höherkristallinen Zustand wurde durch
Temperungsversuche nachgewiesen. Die Löslichkeit des ursprünglichen Polymeren
zeigt daher nur eine geringe Korrelation zu der Löslichkeit der daraus erzeugten Garne.
Hingegen nähert sich die Löslichkeit der getemperten Polymeren viel mehr den an den
hochorientierten Garnen erhaltenen Werten an.