Dependence of the Melting Point of Isotactic Polypropylenes on their Molecular Weight and Degree of Stereospecificity of Different Catalytic Systems

by

G. NATTA, I. PASQUON, A. ZAMBELLI, and G. GATTI

From the Istituto di Chimica Industriale del Politecnico, Milano, and Centro Nazionale di Chimica delle Macromolecole del C.N.R., Milano, Italy

Dependence of the Melting Point of Isotactic Polypropylenes on their Molecular Weight and Degree of Stereospecificity of Different Catalytic Systems

By G. Natta, I. Pasquon, A. Zambelli, and G. Gatti

Dedicated to Prof. Dr. Dr. h.c. K. ZIEGLER on the occasion of his 65th birthday

SUMMARY:

Polymers of propylene having highly regular isotactic structure and low molecular weight (down to about 800) were prepared. The melting point, the X-ray crystallinity, the solubility in some solvents and the molecular weight of each polymer fraction have been determined.

The melting point increases with the increase of the molecular weight until reaching the limiting value for molecular weights of the order of 10^3.

The data have been used in the polymerization of propylene to prove the higher stereospecificity of the catalytic systems based on violet $TiCl_3$ and of one of the following compounds: $Al(C_2H_5)_2I$, $Be(C_2H_5)_2$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2Cl$, in comparison with the corresponding systems prepared with $Al(C_2H_5)_3$.

ZUSAMMENFASSUNG:

Polymere des Propylens mit hochgradig regelmäßiger isotaktischer Struktur und mit niedrigem Molekulargewicht (bis zu etwa 800) wurden hergestellt. Der Schmelzpunkt, die Röntgenkristallinität, die Löslichkeit in einigen Lösungsmitteln und das Molekulargewicht jeder Polymerfraktion wurden bestimmt.

Der Schmelzpunkt steigt mit steigendem Molekulargewicht bis zum Erreichen eines asymptotischen Wertes für Molekulargewichte in der Größenordnung von einigen 10 000.

Die erhaltenen Daten wurden benutzt, um zu beweisen, daß die Katalysatorsysteme, die auf $TiCl_3$ und einer der Verbindungen: $Al(C_2H_5)_2J$, $Be(C_2H_5)_2$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2Cl$ beruhen, stereospezifischer sind als die, bei denen $Al(C_2H_5)_3$ verwendet wird.

1. Introduction

Since the first research on the polymerization of propylene to isotactic polymers it was observed for sufficiently high molecular weights that the solubility of polypropylene in certain solvents was practically independ-

ent of the molecular weight of the polymers and dependent on its steric regularity[1]; therefore, one of us proposed[1,2] to evaluate the stereoregularity of the crude polymers (and consequently the stereospecificity of the catalytic systems used for their preparation) by fractionation made by extraction with different solvents at their boiling temperature. The percentage of the non-extractable fraction in boiling n-heptane of a given sample of polypropylene was called "index of isotacticity".

This method is based on the ascertainment that the presence of a steric irregularity in a stereoregular polymer implies a decrease in melting temperature, similar to the decrease of the melting point in the presence of chemical irregularities e.g., in copolymerization, by statistical introduction of monomeric units which are different in chemical nature and in size from the monomeric units of the polymer considered. Such a variation in the melting temperature can be calculated theoretically on the basis of a formula proposed by Flory[3].

An increase in solubility generally corresponds to a decrease in melting temperature; in fact, with solvents of the same chemical nature (e.g., saturated normal hydrocarbons) used at their boiling temperature for the fractionated extractions, the fractions show an increasing melting temperature with the boiling temperature of the solvent used[1].

Obviously, the polymers melting at higher temperatures show a higher crystallinity, accompanied by better mechanical and thermal properties which determine their possible practical applications. The extraction at temperatures above the boiling temperature of n-heptane generally does not lead to the separation of fractions with melting temperature and crystallinity markedly different from fractions in the residue of the n-heptane extraction; but generally there is a difference in the molecular weights. The melting temperatures of polypropylenes in the residue of the n-heptane extraction may be different only by some degrees (e.g., generally they range from 170 to 177 °C., if determined by the conventional methods). These differences do not cause considerable variations in the technological and, particularly, in the mechanical properties of these fractions. Due to these different reasons, it was justified to consider the fractions left as residue of the heptane extraction of crude polymers as isotactic.

Thus, in most cases the n-heptane extraction of crude polypropylenes allows to obtain approximately a relative measure of the steric purity of a polymer; due to its easy execution, it has been generally accepted and employed by most researchers, especially for routine works.

This method is *a priori* limited by the fact that, below a certain molecular weight, the solubility of the polymer in a given solvent will not only depend on its steric regularity, but also on its molecular weight.

As we observed in a previous paper[4], it is actually possible to prepare isotactic polymers of propylene with very low molecular weight, relatively high crystallinity and soluble not only in boiling n-heptane, but also in boiling ethyl ether.

In these cases and, generally in polymerizations yielding polymers with fractions of molecular weights below a certain value, the evaluation of the degree of steric regularity of the polymer by its index of isotacticity (expressed as % of insoluble polymer in boiling n-heptane) obviously yields too low values.

It must be borne in mind that a direct determination of the steric purity, *e.g.*, based on the number of alternances of steric configurations with respect to the number of repetitions, by nuclear magnetic resonance[5], does not allow a complete characterization of the polymer, particularly as far as crude polymers are concerned. In fact, the same percentage of irregularities can exert a different influence on the physical properties, depending on whether the steric irregularities are randomly distributed in all the molecules or preferentially concentrated in some molecules or in part of them. The same considerations can be made for the melting temperature and for crystallinity.

Crystallinity, which is indubiously the property that mostly influences both mechanical and technological properties of the polymers can be different when measured by X-rays or by I.R. The content of isotactic macromolecules cannot only be determined on the basis of crystallinity measurements of a crude polymer; in fact a certain crystallinity is observed also in the absence of isotactic macromolecules if stereoblock molecules are present.

A better characterization of a crude polymer can be made only by fractionation with different solvents and by the determination of the molecular weights of the various fractions, accompanied by measurements of density, of crystallinity and/or of the melting point of each fraction.

It must be kept in mind that crystallinity depends on the thermal and mechanical history of the sample; therefore, its numerical value is significant only if a particular thermal treatment of the molten polymer is strictly followed.

Moreover, polymers with the same steric regularity, but with very different molecular weights, can show different degrees of crystallinity, even

if determined by the same method, e.g., by X-ray measurements, owing to the different kinetics of crystallization and particularly to the slower crystallization of the polymers with higher molecular weight. Also, the final melting point depends on the thermal treatment of the sample[6].

When the molecular weight decreases below the value for which the influence of the terminal groups can no longer be neglected contrasting phenomena occur: crystallinity decreases owing to the increasing influence of the terminal groups; the crystallization rate increases owing to the shortening of the polymeric chains.

Moreover, it is well known that, below a certain value of their molecular weight, the melting temperature of the polymers decreases also owing to the influence of the terminal groups.

In this paper we shall try to point out the influence of the molecular weight of isotactic polypropylene on its solubility in some solvents, on its melting point and on its crystallinity measured by X-rays. For this purpose, highly isotactic polypropylene samples of different molecular weight, but practically with the same steric regularity have been prepared.

The results obtained have been subsequently used to prove the relative stereospecificity of different catalytic systems based on violet $TiCl_3$ and on some organometallic compounds of aluminum or of beryllium.

2. Preparation of Polypropylenes with Different Molecular Weight and with the Same Steric Regularity

Polymer fractions of lower molecular weight have been prepared by thermal degradation of polymers already possessing a high degree of steric regularity.
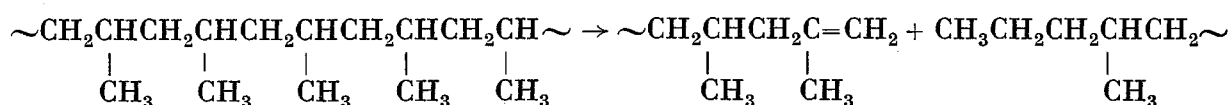
Other samples have been directly synthesized by polymerization in the presence of different concentrations of hydrogen, which acts as chain transfer agent and decreases the molecular weight[7] presumably without reducing the steric regularity of the polymer chains. The operating conditions were those usually allowing the isolation of polymers with very high steric regularity, but in the absence of H_2.

The polymers obtained by thermal degradation, according to the procedures reported in the experimental part, have been first subjected to extraction with methanol at its boiling temperature. The residue was then fractionated by successive extractions with acetone, ethyl ether, n-pentane, n-hexane, and n-heptane.

With acetone and ethyl ether, it was possible to carry out, with each solvent used in subsequent extractions, also a fractionation depending on the molecular weight of the polymer.

The fractions thus separated, derived from the degraded polymers, have been examined by I.R. The spectrum was characteristic of isotactic polypropylene containing vinylidenic terminal groups. The presence of vinyl groups was not observed. Together with other investigations in this direction[8] this makes us believe, that the degradation of the polymer has occurred quite regularly, i.e., with formation of a vinylidenic and an n-propylic end group for each chain rupture:

$$\sim CH_2CHCH_2CHCH_2CHCH_2CHCH_2CH\sim \rightarrow \sim CH_2CHCH_2C{=}CH_2 + CH_3CH_2CH_2CHCH_2\sim$$

$$\underset{CH_3}{|} \quad \underset{CH_3}{|} \quad \underset{CH_3}{|} \quad \underset{CH_3}{|} \quad \underset{CH_3}{|} \qquad \underset{CH_3}{|} \quad \underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$

For statistical reasons the polymers degraded by thermal methods should consist of 50 % by number of macromolecules containing one vinylidenic end group at one end of the chain and one n-propylic group at the other end, of 25 % of chains containing two vinylidenic end groups and of 25 % of chains containing two n-propylic end groups.

Table 1. Characteristics of low molecular weight polymers of propylene with isotactic structure, obtained by thermal degradation of a highly crystalline polymer

Fraction	Solvent used to separate the fraction	Molecular weight[*]	Melting point (°C.)	Crystallinity by X-rays (%)
1	acetone	870	89—90	72
2	acetone	905	92—93	76
4	acetone	930	100—101	85
5	acetone	1050	104—105	92
6	ethyl ether	1340	109—110	85
7	ethyl ether	2000	113—114	86
8	ethyl ether	n.d.	115	n.d.
9	ethyl ether	n.d.	117	n.d.
10	n-pentane	3000	112	79
11	n-hexane	≈ 10000	n.d.	n.d.
12	n-heptane	≈ 14000	154	78
Starting polymer	insoluble in boiling n-heptane	intrinsic viscosity > 10	175	60

[*] The molecular weights of fractions 1—7 were determined with a "Mechrolab"; that of fraction 10 on the basis of the determination of the vinylidenic terminal groups measured by I.R. analysis[9]; those of the fractions 11 and 12 by viscosimetric method[10].

On the basis of these considerations it can be assumed that the polymer fractions thus prepared essentially differ one from another only in their molecular weight.

Moreover, the method used to obtain the different fractions and the relatively small variation of their molecular weight passing from one fraction to the next (see Table 1) make us believe that the distribution of the molecular weights for each fraction is very narrow.

Table 2. Characteristics of isotactic polypropylenes obtained directly by synthesis with the aid of a highly stereospecific catalytic system (violet $TiCl_3-Al(C_2H_5)_2I$)

Polymeri- zation run[a]	Polymeri- zation temp. (°C.)	Solvent used to separate the fraction	Viscosi- metric M.W.	Melting point (°C.)	Crystallinity by X-rays (%)
1	15	n-heptane[b]	12,000	155–156	77
2	84	n-octane[c]	27,000	167	77
3	66	n-octane[c]	83,000	174	75
4	66	n-octane[c]	95,000	174	74
5	66	n-octane[c]	165,000	174	78
6	66	n-octane insoluble	234,000	175	78

a) the polymerization runs 1, 4, 5, and 6 were carried out by operating in the presence of H_2; the polymerization run 2 was carried out by operating with a high concentration of $Al(C_2H_5)_2I$.
b) after n-hexane extraction.   c) after n-heptane extraction.

3. Influence of the Molecular Weight of Isotactic Polypropylene on its Solubility, on the Melting Point and on its X-ray Crystallinity

The results obtained from the measurements on polymer samples are reported in Tables 1 and 2 and in Figs. 1 and 2.

The data show that it is possible to obtain low molecular weight polymers of propylene with isotactic enchainment which are highly crystalline and very soluble (also in acetone).

From the data it can also be observed that with decreasing molecular weight from the value corresponding to the starting polymer the X-ray crystallinity of the single fractions increases up to a maximum and then it decreases again at very low molecular weights ($\approx$ 1000–1100).

This behaviour can be interpreted taking into account that with the decrease of the molecular weight of the polymer, its crystallinity tends to decrease owing to the increasing influence of the end groups, while the crystallization rate increases owing to the higher diffusibility of the macromolecules.

The data show, as it could be foreseen, that the conventional methods for the determination of crystallinity by X-rays do not give data univocally connected with the steric regularity of the samples examined, especially if the range of the molecular weights is very wide and also comprises low molecular weights.

The same considerations are valid both for the determination of crystallinity by I.R. and with the help of density measurements.
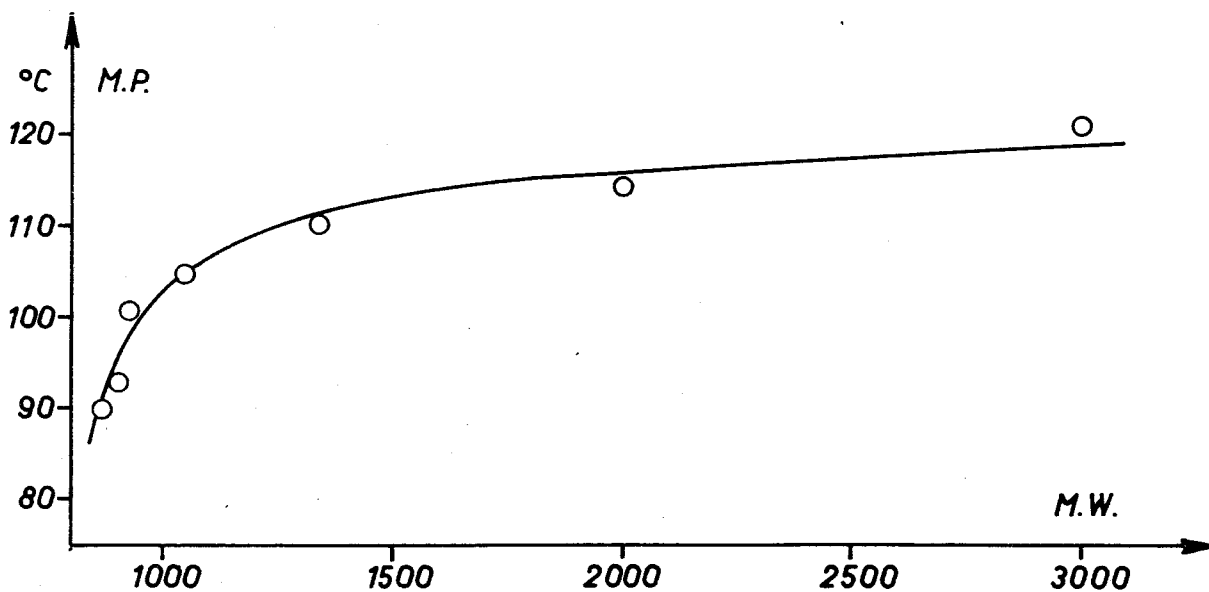

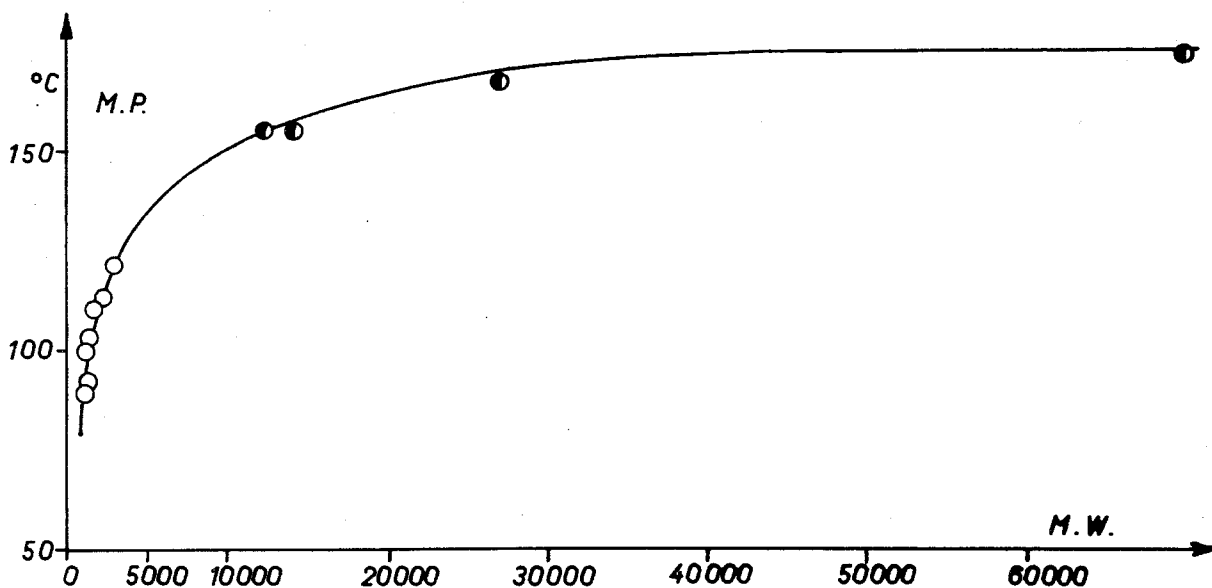Fig. 1. Melting point of isotactic polypropylene *vs.* number molecular weight

Fig. 2. Melting point of isotactic polypropylene *vs.* molecular weight
O number M.W. ● viscosity M.W.

197

The melting points of our polymers with the same steric purity are an increasing function of the molecular weight upto molecular weights of the order of some 10000; for higher molecular weights, the melting point reaches practically a constant value (Fig. 2). It must be observed that the curves reported in Figs. 1 and 2 are characteristic of the polymers examined; for polymers of lower steric regularity, the highest melting point should presumably be reached later, i.e., for molecular weights higher than those observed for the high steric purity products.

Table 3. Polymerization of propylene in the presence of $Zn(C_2H_5)_2$, α-$TiCl_3$ (0.31 g.), $Al(C_2H_5)_3$ (0.45 ml.), n-heptane (250 ml.); t = 70 °C.; $p_{C_3H_6}$ = 960 mm. Hg; polymerization time 1 hr.[11]

$Zn(C_2H_5)_2$ (ml.)	Polymer obtained (g.)	Ether extract (%)	n-heptane extract (%)	residue (%)	[η] of residue of ether extract. (100 ml./g.)	M.W.
0	14.50	11.5	6.5	82.0	3.18	570,000
0.10	14.21	8.5	9.5	82.0	1.58	222,000

Finally, it is observed that for raw polymers with a sufficiently high steric regularity and a molecular weight higher than for instance 50—100,000, the index of isotacticity, defined as percentage of in boiling n-heptane insoluble product can be practically considered as independent of the molecular weight*). This agrees with the data obtained by us in previous research: some of them are reported in Table 3. These data show that by addition of small amounts of $Zn(C_2H_5)_2$, under conditions where this compound acts only as chain transfer agent to the violet $TiCl_3$—$Al(C_2H_5)_3$ system it is possible to decrease the intrinsic viscosity of crude polypropylene from 3.18 to 1.58, without reducing the percentage of polymer left as residue of the boiling n-heptane extraction.

However, it must be observed that the determination of the relative steric regularity of a polymer with a sufficiently high steric regularity, by means of the determination of the index of isotacticity defined above

---

*) For decreasing steric purities, this limit will increase more and more until, for steric purities lower than a certain value, the polymer will be completely soluble in boiling n-heptane, independently of its molecular weight. In fact, a previous paper[12] already reports examples of polypropylenes with very low steric regularity, which are soluble in n-heptane and have a molecular weight of the order of some 100,000.

will give values that are the more inaccurate the more the considered polymer will contain higher proportions of macromolecules of molecular weight lower than 10—20,000 [*].

Finally, the different results reported so far show that in many cases it is possible to attain, to a good approximation, an evaluation of the relative steric regularity of different polymers, if solubility data are associated with measurements of molecular weights and of melting points.

Table 4. Relative stereospecificity of catalytic systems in the polymerization of propylene. t = 70 °C.; α-TiCl$_3$ (0.746 g.); organometallic compound (2 ml.), toluene (250 ml.)

Organo-metallic compound	p$_{C_3H_6}$ (mm. Hg)	Polymerization time (hr.)	Polymer obtained							
			Raw			ether extract (%)	n-hept. extract (%)	Residue		
			(g.)	[η]	M.W.			(%)	[η]	M.W.
Be(C$_2$H$_5$)$_2$	1200	$^3/_4$	21.0	2.85	490,000	3.0	3.0	94.0	2.90	500,000
Al(C$_2$H$_5$)$_3$	1450	2	20.5	3.15	560,000	11.0	7.5	81.5	3.90	740,000

4. Relative Stereospecificity of some Catalytic Systems for the Polymerization of Propylene

In the light of the results reported in this paper, we have taken into new consideration some data we obtained long ago — which have been published only partly so far[2,4] — concerning the relative stereospecificity of some catalytic systems for the polymerization of propylene to isotactic polymers.

Table 4 shows some results concerning experimental runs carried out with the use of violet TiCl$_3$—Al(C$_2$H$_5$)$_3$ and of violet TiCl$_3$—Be(C$_2$H$_5$)$_2$ systems.

From these data it can be observed that the polymer obtained with the use of the system based on Be(C$_2$H$_5$)$_2$ exhibits a higher percentage of residue of the n-heptane extraction and a molecular weight that is lower than for the polymer obtained with the use of the system based on Al(C$_2$H$_5$)$_3$; this shows, in proof of a previous paper by one of us[2] and in contrast to what was recently proposed by others[13], that the catalytic system violet TiCl$_3$—Be(C$_2$H$_5$)$_2$ is more stereospecific than the system violet TiCl$_3$—Al(C$_2$H$_5$)$_3$.

---

[*] This is, for example, the case of polymers obtained with the use of systems based on α-TiCl$_3$—Al(C$_2$H$_5$)$_3$ in the presence of increasing amounts of Zn(C$_2$H$_5$)$_2$ or of H$_2$; in fact, these last compounds act as chain transfer agents and, if used in sufficiently high amounts, can originate considerable decreases in the molecular weights[11,7].

It is also interesting to compare the results obtained with violet $TiCl_3$ in the presence of one of the following organometallic compounds of aluminum: $Al(C_2H_5)_2I$, $Al(C_2H_5)_2Br$, $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)_3$.
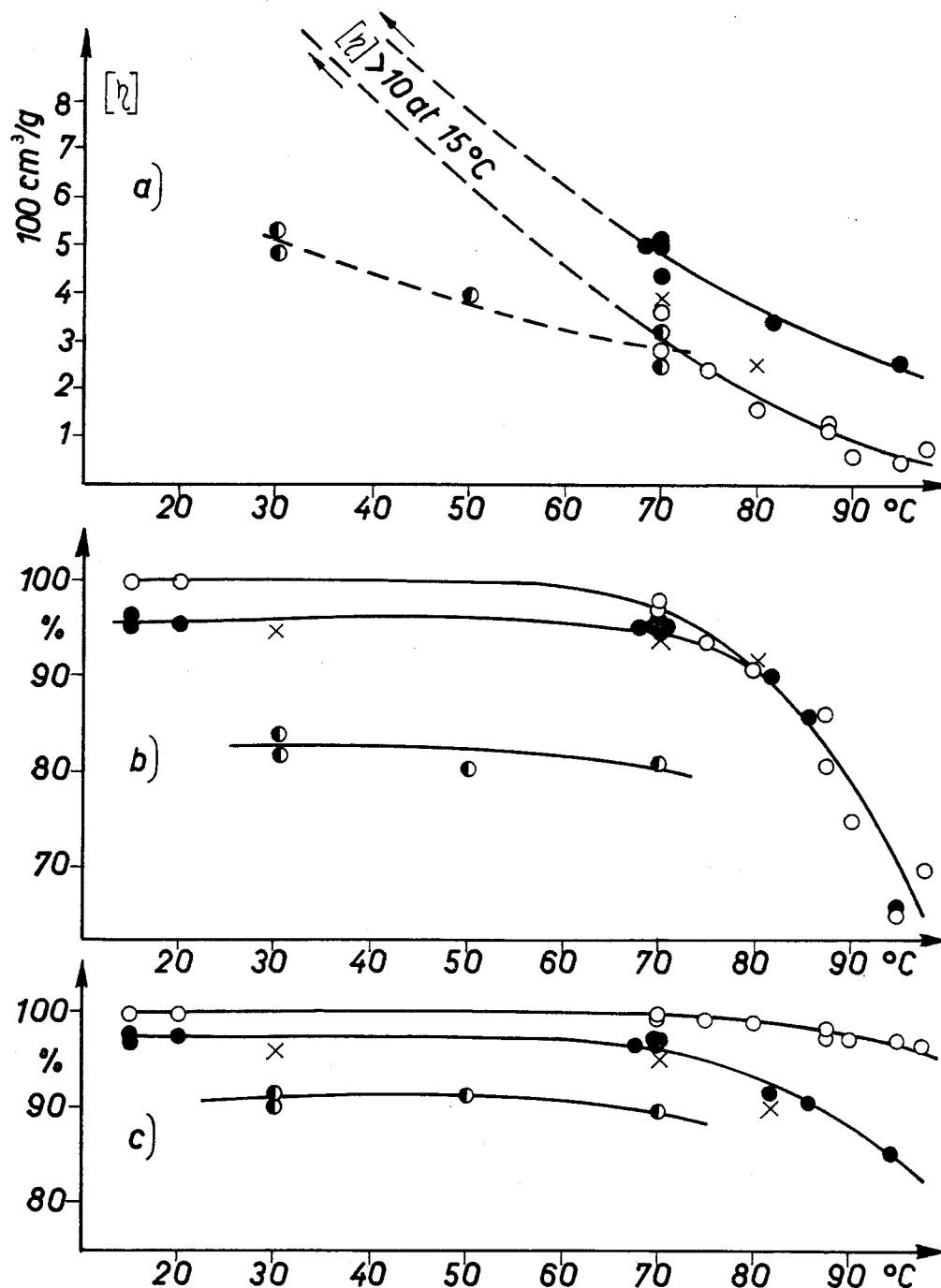

Fig. 3. Comparison of the intrinsic viscosities of polypropylenes obtained at different polymerization temperatures in the presence of catalytic systems based on violet $TiCl_3$ and organometallic compounds

(Violet $TiCl_3$: 10—15 mmole/l.; $Al(C_2H_5)_2X$: 25—35 mmole/l.; $p_{C_3H_6}$: 2—3 atm.; solvent: n-heptane)

a) Intrinsic viscosity; b) residue of boiling n-heptane extraction; c) % residue of ethyl ether extraction

$\circ$ $Al(C_2H_5)_2I$, $\quad\times$ $Al(C_2H_5)_2Cl$, $\quad\bullet$ $Al(C_2H_5)_2Br$, $\quad\mathbb{O}$ $Al(C_2H_5)_3$

The data reported in Fig. 3 show that the molecular weight of the crude polymer obtained in the presence of $Al(C_2H_5)_2Br$ is always higher than that of the polymer obtained at the same temperature with $Al(C_2H_5)_2I$; nevertheless, for products obtained with this last catalytic system at temperatures lower than about 80 °C., the polymer residue of the n-heptane extraction is higher. By operating at temperatures higher than 80 °C., e.g., 95 °C., it is possible, with the use of the system containing $Al(C_2H_5)_2I$, to obtain crude polymers with very low intrinsic viscosity ($[\eta] \geqslant 0.5$) and a very high percentage of residue of the ethyl ether extraction ($> 96\%$); on the contrary, the polymer obtained by operating under the same conditions, but with the $Al(C_2H_5)_2Br$ system, has an intrinsic viscosity of about 2.5 and a residue of the ethyl ether extraction not higher than 85%. The increase in the percentage of polymer extractable with boiling n-heptane, observed at polymerization temperatures higher than 70—75 °C., must be attributed both to the fact that, with increasing temperature the percentage of very low molecular weight polymer increases, and that the stereospecificity of the catalytic system decreases (depending on the different systems).

Moreover, it must be taken into account that both the ether and the heptane soluble fractions of polypropylenes obtained with the systems based on $Al(C_2H_5)_2I$ are crystalline even if they are obtained by runs performed at the highest experimental polymerization temperatures[4].

These data further confirm the highest stereospecificity of the catalytic systems based on $Al(C_2H_5)_2I$ in comparison to the systems based on $Al(C_2H_5)_2Br$ or on the other organometallic compounds of aluminum considered here[4].

The data reported in Fig. 3 also show that, even if the polymers obtained at 70 °C. under the conditions described and in the presence of the different systems have almost the same molecular weights, the percentage of residue of the n-heptane or ether extractions is considerably different. This result, too, shows that the determination of the index of isotacticity (particularly if it is associated with measurements of molecular weight), at least in several cases, represents a satisfactory criterion to evaluate the relative stereospecificity of the different catalytic systems.

Finally, we wish to notice that an accurate and detailed interpretation of the experimental data concerning the stereoregularity of the polymers obtained with different organometallic compounds is not only important from the point of view of applications, but also for a correct interpretation of the polymerization mechanism of propylene to isotactic polymer, with particular reference to the knowledge of the nature of the catalytic complexes.

5. Conclusions

By thermal degradation of isotactic polypropylenes having high molecular weight and high steric purity, low molecular weight polymers have been obtained, which, regardless of the end groups, show the same steric purity as that of the chain of the starting polymers.

The melting temperature, the solubility and the crystallinity of fractions with a narrow distribution of the molecular weights, obtained by fractionation with solvents, have been determined. With regard to low molecular weight polymers, the melting temperature varies from 89 to 150 °C. for a corresponding variation of the molecular weight from 870 to 10,000. With a further increase of the molecular weight, the variation of the melting temperature is more limited (from 168 to 175 for viscosimetric molecular weights ranging from about 30,000 to 100,000). Crystallinity increases with the decrease of the molecular weight until *ca.* 1000, but it decreases when the molecular weight decreases further owing to the higher influence of the terminal groups. Fractions with a molecular weight higher than some 10,000 are insoluble in boiling heptane, whereas the polymers with a molecular weight ranging from 10,000 to about 15,000 are soluble in heptane, those with a molecular weight lower than *ca.* 10,000 are soluble in hexane, and those with a molecular weight lower than 1,300 are soluble in ethyl ether, even if they are all highly crystalline.

This proves that in polypropylenes with a molecular weight higher than ca. 30,000, solubility depends more on the steric regularity than on the molecular weight, and that the determination of the percentage of boiling *n*-heptane insoluble product can be adopted as a criterion to determine the percentage of isotactic polymer present in the sample examined, and as a comparative method to determine the stereospecificity of a given catalytic system.

Different catalytic systems have been compared; it was confirmed that those based on violet $TiCl_3$ and $Al(C_2H_5)I$ are the most stereospecific known and that the systems based on $Be(C_2H_5)_2$ are more stereospecific than those based on $Al(C_2H_5)_3$.

6. *Experimental Part*

1. *Preparation of low molecular weight polymers*

a) Products obtained by thermal degradation of stereoregular high polymers

The starting polymer was obtained by polymerizing propylene at 15 °C. with the aid of the catalytic system δ-$TiCl_3$ (containing $AlCl_3$ in solid solution) — $Al(C_2H_5)_2I$ in toluene at 6 atm. of monomer pressure. The polymer thus obtained was 100 % insoluble in boiling n-heptane and had an intrinsic viscosity > 10, melting temperature of 175 °C. and an X-ray crystallinity of 60 %.

The polymer thus prepared was thermally degraded by flash heating of samples placed in a glass flask maintained at 20 mm. Hg. On heating the polymer distilled and was collected in a flask maintained in an inert medium.

The distillate was extracted preliminary in a KUMAGAWA extractor with boiling methanol in order to exclude the lower and more irregular fractions *).

The successive fractionation was carried out in a KUMAGAWA extractor, removing the extracted fractions at intervals ranging from 15 to 24 hrs.

When the solvent used for a series of subsequent extractions did not extract any more polymer, it was substituted by another solvent able to extract a new series of fractions.

The results obtained from these runs are reported in Table 1.

b) Polymers directly obtained in polymerization runs

Some low molecular weight polymer fractions have been obtained directly from polymerization runs performed in the presence of hydrogen with the catalytic system violet $TiCl_3$–$Al(C_2H_5)_2I$. The polymerizations were carried out at 15° and 66 °C., in a 500 ml. autoclave, following the methods described in a previous paper [14].

The polymers obtained in these runs were fractionated by solvent extraction. Table 2 reports some operating conditions and the most significant results for this paper, obtained in these runs.

2. *Polymerization runs*

The polymerization runs carried out with the aid of the different catalytic systems mentioned in the various tables were all carried out at constant temperature and pressure for the whole period of the run, following the operating procedures described in a previous paper [14].

3. *Reagents Used*

Solvents

Toluene and n-heptane used in the polymerization runs were the usual commercial products previously anhydrified by boiling on metallic potassium and distilled under nitrogen atmosphere.

---

*) Boiling methanol can also extract highly crystalline polymer fractions of lower molecular weight than taken into account in this paper.

Monomer

The monomer used, supplied by Montecatini, had a propylene content $\geqslant 98\%$, the impurities present being almost exclusively propane.

Components of the catalytic system

Violet $TiCl_3$ in the α, γ or δ modifications was used in the polymerization runs. As it is known, the stereospecificity of the catalytic systems prepared from violet $TiCl_3$ does not depend on the α, γ or δ modification[4]. The $TiCl_3$ was purified by washing with hydrocarbons in an extractor, following the procedures described in a previous paper[4].

The method of preparation and the degree of purity of the organometallic components used are quoted or reported in a previous paper[4].

4. Examination of the polymers

Molecular weights

The molecular weights of the fractions of lower molecular weight were determined with a "Mechrolab" by the Montecatini Laboratories at Castellanza to whom we would like to express our gratitude. The molecular weights of higher fractions have been determined by viscometric methods in tetralin at 135 °C.[10] or by I.R. measurements[9].

Melting points

The melting points have been determined with a polarizing light microscope at a heating rate of 1 °C./5 min.

Crystallinity

The X-rays crystallinity of the fractions was determined according to Natta and co-workers[15].

The crude degraded polymer shows, by X-rays, a spectrum characteristic of modification γ[16]. After solution and reprecipitation with methanol, the X-ray spectrum becomes equal to that of the more stable monocline modification. Before starting the measurement of crystallinity, the samples were annealed at a temperature of about 20 °C lower than the melting temperature.

A small influence of annealing on the low molecular weight polymers has been observed. For polymers of higher molecular weight, annealings were done until reaching a constant crystallinity.

I.R. analysis

The I.R. analysis of the reported fractions of degraded polymer allows to observe only the presence of double bonds of the vinylidenic type. The quantitative determination was accomplished by operating with polymer solutions in carbon tetrachloride, with known content of these double bonds on the basis of the absorption intensity at 11.27 μ (assuming the average value of the absorption coefficient of the vinylidenic groups)[9]. A Perkin-Elmer double beam spectrophotometer with NaCl optics was used.

[1] G. Natta, Atti Accad. naz. Lincei, Mem. **352** (8) (1955) 61; G. Natta, G. Mazzanti, G. Crespi, and G. Moraglio, Chim. e Ind. [Milano] **39** (1957) 275.

[2] G. Natta, Experientia [Basel] Suppl. **7** (1957) 21; J. Polymer Sci. **34** (1959) 21.

[3] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca 1953.

[4] G. Natta, I. Pasquon, A. Zambelli, and G. Gatti, J. Polymer Sci. **51** (1961) 387.

[5] A. Miyake and R. Chûjô, J. Polymer Sci. **46** (1960) 163; S. Satoh, R. Chûjô, T. Ozèki, and E. Nagai, J. Polymer Sci. **62** (1962) S101.

[6] H. W. Wyckoff, J. Polymer Sci. **62** (1962) 83.

[7] G. Natta, G. Mazzanti, P. Longi, and F. Bernardini, Chim. e Ind. [Milano] **41** (1959) 519.

[8] T. E. Davies, R. L. Tobias, and E. B. Peterli, J. Polymer Sci. **56** (1962) 485; J. V. van Schooten, and P. W. O. Wijga: paper presented at the Symposium of the Plastics and Polymer Group, 21–23 Sept. 1960, London.

[9] H. L. Mc Murray and V. Thornton, Analytic. Chem. **24** (1952) 318.

[10] G. Moraglio, Chim. e Ind. [Milano] **41** (1959) 879.

[11] G. Natta, E. Giachetti, I. Pasquon, and G. Pajaro, Chim. e Ind. [Milano] **42** (1960) 109.

[12] I. Pasquon, Chim. e Ind. [Milano] **41** (1959) 534.

[13] A. P. Firsov, B. N. Kashprov, Yu. V. Kissin, and N. M. Chirkov, J. Polymer Sci. **62** (1962) S104.

[14] G. Natta, I. Pasquon, and E. Giachetti, Angew. Chem. **69** (1957) 213.

[15] G. Natta, P. Corradini, and M. Cesari, Rend. Accad. naz. Lincei, Mem. **22** (8) (1957) 11.

[16] E. J. Addink and J. Beintema, Polymer [London] **2** (1961) 185.