

Thermal behaviour of highly stereoregular syndiotactic polypropene from homogeneous catalysts

Giulio Balbontin*, Dario Dainelli^{a)}, Maurizio Galimberti*

HIMONT Italia S. r. l., Via Caduti del Lavoro, I-28100 Novara, Italy

Guglielmo Paganetto

HIMONT Italia S. r. l., Centro Ricerche G. Natta, I-44100 Ferrara, Italy

(Date of receipt: February 2, 1991)

SUMMARY:

Thermal characterization was carried out on highly stereoregular and regioregular syndiotactic polypropene (sPP) obtained with isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane. The influence of molecular weight and syndiotacticity degree on the thermodynamic melting point (T_m^0) of sPP were separately investigated by examining samples with a fully syndiotactic pentads content ($rrrr$) ranging from ca. 81% to ca. 94% and with an weight-average molecular weight (\bar{M}_w) ranging from $9,6 \cdot 10^4$ to $17,3 \cdot 10^4$. Upon excluding any influence of the molecular weight, the correlation between the $rrrr$ pentads content and the T_m^0 of the samples led to the extrapolation of the thermodynamic melting point for a fully syndiotactic polypropene.

Introduction

It is well known that the stereoisomerism, as well as other molecular characteristics, such as molecular weight, greatly influence the physical and mechanical properties of polymers. Such influence has to be considered along with those exercised by bulk scale parameters like molecular-weight distribution (MWD) and amorphous/crystalline content ratio. All these factors affect the crystal morphology of the polymers and influence the properties of the materials by changing the crystal form and/or perfection.

The possibility of modulating the stereoisomerism of the polymers by modifying the catalyst has been largely used up to now in order to obtain many polymers with different degrees of stereoregularity.

Polypropene in the isotactic configuration (iPP), first obtained by Natta et al.¹⁾ is nowadays produced with a very high degree of stereoregularity (isotactic index $> 98\%$)²⁾ and represents one of the most versatile thermoplastics available because of its optimum ratio between cost and physico-chemical properties.

Isotactic polypropene has been widely characterized until now. Accurate information concerning the morphology and the crystallization behaviour has been reported^{3–5)}.

Syndiotactic polypropene (sPP) was also synthesized by Natta et al.⁶⁾ This sPP has a stereoblock structure with syndiotactic sequences prevailing to isotactic ones (about 70% of syndiotactic triads)⁷⁾ and head-to-head/tail-to-tail regioirregular defects.

^{a)} Present address: Cryovac-Grace Italiana, Via Trento 7, I-20017, Passirana di Rho (MI), Italy.

Data concerning the thermal properties and the crystalline habitus of this sPP have been published⁸⁻¹⁴.

As recently reported, the synthesis of highly stereoregular and regioregular sPP has been achieved by Ewen using a catalytic system composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium or hafnium dichloride and methylaluminumoxane¹⁵.

We have recently started studies on sPP obtained with the Ewen's catalyst in order to obtain information on the structure-properties relationships for this potentially interesting material. This paper concerns in the thermal properties of syndiotactic polypropylenes of different molecular weight and degree of stereoregularity. The melting behaviour of the isothermally crystallized samples was analysed in order to study the dependence of the equilibrium melting temperatures (T_m^0) on both the molecular weight and the tacticity. For a fully syndiotactic polypropene the equilibrium melting temperature (T_m^0)_{100%} as well as the enthalpy of fusion (ΔH_u) were estimated.

Results and discussion

Synthesis and solution characterization

In Tabs. 1 and 2 the results of the polymerization and the properties of the obtained polypropylenes are summarized. Samples of sPP were obtained with the weight-average molecular weight \bar{M}_w ranging from ca. $50 \cdot 10^3$ to $260 \cdot 10^3$ and with very similar molecular weight distribution MWD. ¹³C NMR analysis shows that all the polymers are highly syndiotactic. The fully syndiotactic pentads¹⁶ are indeed in the range of ca. 94% for sample 1 to ca. 81% for sample 6. No peaks due to head-to-head propylene sequences are detectable in any of the spectra for the sPP samples, indicating that only defects due to stereoirregularity are present along the macromolecular chain. Furthermore, the absence of *mmmm* and *mmm*r pentads suggests a substantially random distribution of the isotactic units in an essentially syndiotactic chain. A parallel trend is observed between the values of molecular weight and syndiotacticity. The

Tab. 1. Conditions of the polymerization of propene using isopropylidene(cyclopentadienyl)-(9-fluorenyl)zirconium dichloride and methylaluminumoxane $[-Al(CH_3)-O-]_n$ as catalytic system

Exp. No.	Catalyst amount in mmol ($\times 10^3$)	Mole ratio Al/Zr	Solvent type	Solvent amount in mL	Propene pressure in bar	Temp. in °C	t/s	Activity in g of product/mmole of cat.
1	5,78	620	toluene	100	1,7	0	7 200	$1,04 \cdot 10^6$
2	18,50	1 020	toluene	800	4,0	11	14 400	$1,14 \cdot 10^5$
3	9,48	2 050	toluene	750	6,0	80	10 800	$1,40 \cdot 10^4$
4	6,47	1 610	toluene	400	4,5	40	6 120	$5,40 \cdot 10^4$
5	2,01	1 000	pentane	40	4,0	44	1 800	$3,97 \cdot 10^3$
6	2,01	1 000	pentane	40	4,0	60	1 800	$2,45 \cdot 10^3$

Tab. 2. Characterization of the polypropene samples obtained using isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane $[-Al(CH_3)_2-O-]_n$ as catalytic system

Sample ^{a)} No.	η_{inh}^b (dL/g)	\bar{M}_w^c ($\times 10^4$)	\bar{M}_w/\bar{M}_n^c	Pentads distribution in % ^{d)}						
				<i>rmmr</i>	<i>mmrr</i>	<i>xmrx</i>	<i>rrmr</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrrm</i>
1	1,78	26,6	2,6	0,7	1,6	1,0	—	94,5	1,7	0,6
2	1,60	22,8	2,4	0,9	2,1	0,8	—	93,2	2,3	0,7
3	1,20	16,4	2,2	1,3	2,6	1,3	—	92,1	2,4	0,3
4	0,74	7,7	2,9	1,5	3,3	2,3	0,8	88,8	3,1	0,4
5 ^{e)}	0,98	11,5	2,7	1,6	3,1	3,5	—	88,6	2,8	0,4
6 ^{e)}	0,59	5,2	2,3	1,9	4,1	8,5	—	81,4	3,9	0,3

a) The numbers of the samples are those of the corresponding experiments.

b) The inherent viscosity was measured in tetraline at 135 °C.

c) The weight-average molecular weight and the ratio of weight- to number-average molecular weight were determined by GPC.

d) Determined by ^{13}C NMR.

e) Fraction insoluble in boiling diethyl ether and soluble in boiling heptane.

fractionation of sample 3 afforded fractions with different molecular weights but very similar syndiotacticity. The characterization of the fractions is reported in Tab. 3. Fractions with \bar{M}_w ranging from $6,4 \cdot 10^4$ to $17,3 \cdot 10^4$ and very similar molecular-weight distribution were obtained. ^{13}C NMR analysis shows substantially the same pentads distribution for all fractions. All these results indicate that the fractionation was performed only by molecular weight and that the sample was sterically homogeneous. These results agree with those reported by Galambos et al.¹⁷⁾, who used a different fractionation technique, and agree also with the results published by Kashiwa for an isotactic polypropene synthesized with a homogeneous catalytic system¹⁸⁾.

Tab. 3. Properties of the fractions obtained from the fractionation of sample 3

Frac- tion ^{a)}	Wt.-% ^{b)}	η_{inh}^c (dL/g)	\bar{M}_w^d ($\times 10^4$)	\bar{M}_w/\bar{M}_n^d	pentads distribution in % ^{e)}					
					<i>rmmr</i>	<i>mmrr</i>	<i>xmrx</i>	<i>rrrr</i>	<i>rrrm</i>	<i>mrrm</i>
A	100,0	1,20	16,4	2,2	1,3	2,6	1,3	92,1	2,4	0,3
B	5,8	n. d.	6,4	4,6	1,3	3,1	1,8	90,3	2,9	0,6
C	7,2	n. d.	9,6	2,9	1,2	2,6	1,3	91,5	2,7	0,7
D	82,2	1,16	15,2	2,1	1,1	2,5	1,2	91,4	3,0	0,7
E	3,7	1,37	17,3	2,0	1,1	2,3	1,2	91,5	3,2	0,7

a) A: Total polymer; B: soluble in boiling hexane. Extraction with boiling heptane at different partial pressures: C at 213 Torr (82 °C), D at 410 Torr (88 °C), E at 760 Torr; F (1,1%): soluble in boiling toluene.

b) 100 (weight of the fraction/weight of total polymer).

c) Inherent viscosity measured in tetraline at 135 °C.

d) Weight-average molecular weight and ratio of weight- to number-average molecular weight were determined by GPC.

e) Determined by ^{13}C NMR.

Crystallization behaviour

The isothermal kinetic data of sPP were analyzed according to the modified Avrami equation¹⁹. A single crystallization kinetic with one Avrami exponent (n) was observed. The n values were substantially invariant with the crystallization temperature. The data for all samples are listed in Tab. 4. The n values range between about 2,5 and 3,7, with the exception of sample 6, which has an n value between 1,8 and 2,3. This would imply that the crystal growth is tridimensional at least for samples 1–5. These data were supported by preliminary optical microscopic observations. It could be noted that a spherulitic morphology was also found for melt-grown isotactic polypropene²⁰. Tab. 4 shows the inverse of the half time of crystallization $(t_{1/2})^{-1}$ ²¹). This value clearly decreases when the crystallization temperature is increased. The values of the rate constants of the Avrami equation (k) are obtained parallel to those of $(t_{1/2})^{-1}$ as expected. Finally, using the values of the thermodynamic melting point T_m^o (the estimation is reported in the next section), the values of k were plotted versus the supercooling ($\Delta T = T_m^o - T_c$) (Fig. 1). At constant supercooling k increases from sample 1 to 5 while the behaviour of sample 6 is again anomalous.

Melting behaviour

The DSC curves, so far reported in the literature for sPP samples slowly crystallized from the melt, showed more than one fusion peak. These were attributed to the presence of low-molecular-weight fractions as well as of the isotactic phase along with the syndiotactic one¹⁴). On the other hand, the DSC curve of all our samples showed a

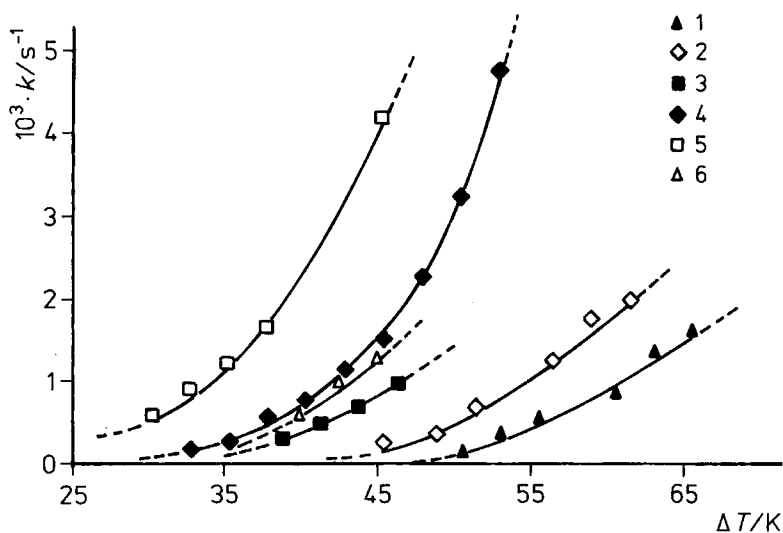


Fig. 1. Avrami kinetic constant k of syndiotactic polypropene samples as a function of the supercooling ($\Delta T = T_m^o - T_c$)

Tab. 4. Overall crystallization data for syndiotactic polypropene samples a)

Sample	1		2		3		4		5		6	
	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$	n	$\frac{10^3 \cdot k}{s^{-1}} \cdot (t_{1/2})^{-1}$
363,1	—	—	—	—	—	—	—	—	—	—	2,27	1,30
365,6	—	—	—	—	—	—	—	—	—	—	1,81	1,00
368,1	—	—	—	—	—	—	—	—	—	—	2,30	0,62
373,1	—	—	—	—	—	—	—	—	—	—	—	—
375,6	—	—	—	—	—	—	—	—	3,38	4,77	5,20	—
378,1	—	—	—	—	—	—	2,30	4,20	3,09	3,25	3,80	—
380,6	—	—	—	—	—	—	—	—	3,18	2,28	2,60	—
383,1	—	—	—	—	—	—	—	—	3,06	1,52	1,70	—
385,6	—	—	—	—	—	—	—	—	3,30	1,16	1,30	—
388,1	—	—	—	—	—	—	—	—	—	—	—	—
390,6	—	—	—	—	—	—	—	—	3,00	1,67	1,95	—
393,1	2,80	1,64	1,95	3,86	2,01	2,23	2,90	0,98	1,12	—	—	—
395,6	2,80	1,38	1,62	3,31	1,79	2,00	3,10	0,70	0,79	—	—	—
398,1	3,00	0,89	1,05	3,95	1,25	1,38	3,40	0,53	0,59	—	—	—
400,6	—	—	—	—	—	—	3,40	0,33	0,38	—	—	—
403,1	2,70	0,59	0,69	3,39	0,69	0,78	—	—	—	—	—	—
405,6	2,00	0,42	0,56	3,32	0,38	0,42	—	—	—	—	—	—
408,1	3,20	0,16	0,18	—	—	—	—	—	—	—	—	—
409,1	—	—	—	2,78	0,28	0,32	—	—	—	—	—	—

a) n = Avrami exponent; k = rate constant of the Avrami equation; $(t_{1/2})^{-1}$ = inverse of the half time of crystallization.

single endotherm upon reheating after the isothermal crystallization as expected from the aforementioned results of ^{13}C NMR and GPC analysis. In fact, the substantially random distribution of the isotactic diads in the syndiotactic chain cannot allow the formation of isotactic crystals as confirmed by X-ray analysis. In the spectrum of sample 3, only peaks due to the orthorhombic cell of sPP were present²²). Furthermore, the narrow MWD excludes the presence of fractions having molecular weights very different from each other.

For every sample, melting points (T_m) for a series of crystallization temperature (T_c) were obtained. The data were analysed according to the Hoffman and Weeks theory²³), which correlates T_m to T_c by the equation:

$$T_m = [(a - 1)/a] \cdot T_m^\circ + (1/a)T_c \quad (1)$$

where T_m° is the thermodynamic melting point and a is the ratio of the average final value of the thickness of a secondary nucleus over the initial thickness. The intersection of the straight line represented by Eq. 1 with the line $T_m = T_c$ provides the values of T_m° and $1/a$. These values for samples 1–6 are reported in Tab. 5 as well as the correlation coefficient for the corresponding least square lines represented in Fig. 2.

Tab. 5. Thermodynamic melting points (T_m°) and $1/a$ as parameters of the Hoffman-Weeks equation for syndiotactic polypropylene samples

Sample	% rrrr	% rr	% r	$T_m^\circ/\text{K} (\pm 3)$	$1/a$	Corr. coeff. ^{a)}
1	94,5	96,7	98,0	459	0,49	0,973
2	93,2	96,2	97,6	455	0,43	0,992
3	92,1	94,8	96,8	439	0,41	0,989
3C ^{b)}	91,5	94,9	96,9	439	0,42	0,995
3D ^{b)}	91,4	95,1	97,0	437	0,39	0,982
3E ^{b)}	91,5	95,4	97,2	443	0,43	0,993
4	88,8	92,2	95,4	423	0,35	0,994
5	88,6	91,8	95,1	426	0,40	0,993
6	81,4	85,6	91,9	408	0,48	0,996

a) Correlation coefficient among the melting points T_m for a series of crystallization temperatures T_c .

b) C, D, E: See footnote^{a)}, Tab. 3.

These lines may be subdivided in four distinct families: samples 1 and 2 having $T_m^\circ = 459$ K and 455 K, respectively, sample 3 having $T_m^\circ = 440$ K, samples 4 and 5 having $T_m^\circ = 426$ K and 423 K, respectively, and sample 6 having $T_m^\circ = 408$ K. All the samples differ both in molecular weight and in degree of syndiotacticity (Tabs. 2, 3 and 5). The classical theory concerning the influence of molecular weight on T_m of polymers states that this influence is expected to be severely diminished as the degree of polymerization is increased²⁴), as it turns out from what reported in the literature for isotactic polypropylene with molecular weight above 15000²⁵). The \bar{M}_w of our samples range between $5,2 \cdot 10^4$ and $26,6 \cdot 10^4$ supporting the assumption that the data

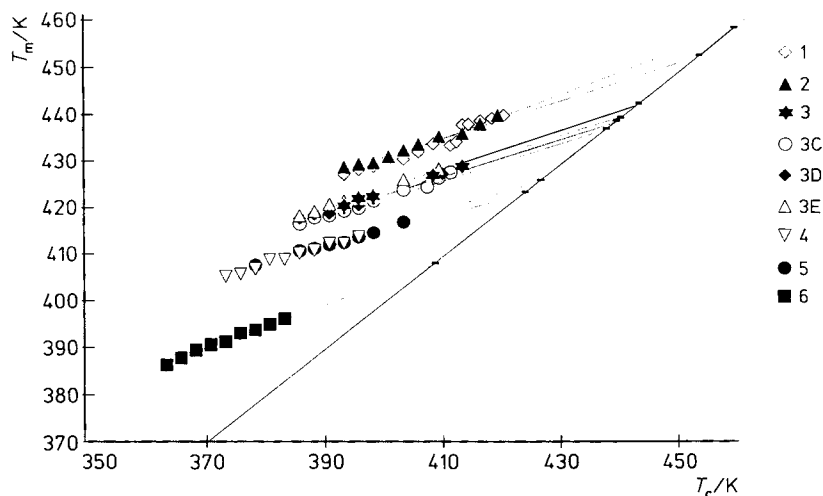


Fig. 2. Melting point (T_m) as a function of the crystallization temperature (T_c) for syndiotactic polypropene samples. The least square lines fit to the points intersect the $T_m = T_c$ line at T_m° (Tab. 5)

are in a "plateau zone". In order to confirm that, we examined the fractions of sample 3, which have similar degree of syndiotacticity but different molecular weights (Tab. 3). The difference in the values of T_m° is slight, ranging from 437 K to 443 K for molecular weights from $9,6 \cdot 10^4$ to $17,3 \cdot 10^4$, respectively. Moreover, samples 4 and 5, which have a comparable degree of syndiotacticity but different \bar{M}_w , show a difference of only three degrees between the values of T_m° . Hence, we can conclude that for our samples the influence of the molecular weight on the T_m° , at least in the experimental range explored, can be disregarded. This conclusion allows us to consider uniquely the effect of the degree of syndiotacticity on the thermodynamic melting point of the samples, exploring a region of very high values of syndiotacticity. The data reported in Tab. 5 suggest that the stereoregularity affects T_m° to a considerable extent.

The T_m° values are linearly correlated to the syndiotacticity degree expressed either as a percent of diads *r* or triads *rr* or pentads *rrrr*. The least square lines were obtained considering only the points with a high correlation coefficient, thus neglecting the contribution of sample 6 (Fig. 3). A previous T_m° value of 431 K was reported for a sPP sample from a Vanadium based homogeneous catalyst¹²⁾ having 72% as *rr* triads content. This T_m° value would correspond to a *rr* triads content higher than 90% according to the corresponding line of Fig. 3. This considerable difference may be explained taking into account the stereoblock nature of sPP obtained from Vanadium catalysts. Moreover, recent studies¹⁴⁾ showed that, with this catalyst, separated isotactic and syndiotactic chains are produced as an intermolecular blend. The degree of syndiotacticity might be then higher than reported. The three straight lines of Fig. 3 intersect the T_m° axis, corresponding to 100% of syndiotacticity, in a range between

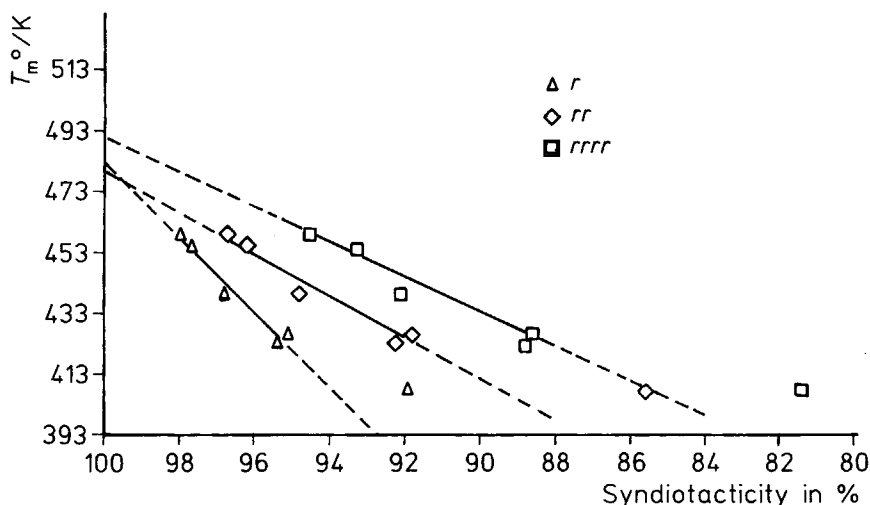


Fig. 3. Thermodynamic melting temperatures (T_m°) as a function of the syndiotacticity expressed as percent of diads (r), triads (rr) and pentads ($rrrr$). The least square lines fit to the points intersect the 100% of syndiotacticity axis giving (T_m°)_{100%} values: 482 K, 480 K, 492 K

481 K and 492 K. Taking into account that the slope of the corresponding lines decreases from the diads to the pentads, a value close to 492 K could be expected even if the ^{13}C NMR analysis would be carried out on longer configurational relationships.

The dependence of T_m° on the syndiotacticity was also treated according to the Flory theory for the depression of melting point in copolymers²⁶⁾, modified for stereoregular polymers^{27, 28)}. The model considers the polymers as a copolymer consisting of r units (syndiotactic diads) which crystallize and m units (isotactic diads) which act as non-crystallizable components. If the two units occur in random sequence, just as in this case, the equation is:

$$1/T_m^\circ - 1/(T_m^\circ)_{100\%} = -(R/\Delta H_u)\ln X_r \quad (2)$$

where (T_m°)_{100%} is the thermodynamic melting temperature for a completely syndiotactic polymer, and X_r is the fraction of the monomer units which are syndiotactically bonded, here expressed as the percentage of r diads. Plotting the experimental values $1/T_m^\circ$ versus $-\ln X_r$ (Fig. 4) one can again estimate (T_m°)_{100%} and the heat of fusion per monomer unit ΔH_u . Neglecting the data of sample 6, the points have a fair correlation. From the slope of the least square line we obtain a value of ΔH_u of 1,4 kJ/mol and (T_m°)_{100%} of 487 K.

The T_m° value for a fully syndiotactic polypropene can be thus presumed to be not far from 493 K. This value agrees with that reported by Miller et al.¹²⁾ For an isotactic polypropene having isotacticity index higher than 99%, Cheng et al.²⁵⁾ reported a T_m° value of 458 K. Although this value is still somewhat uncertain, according to this work the syndiotactic polypropene seems to have a higher thermodynamic melting point.

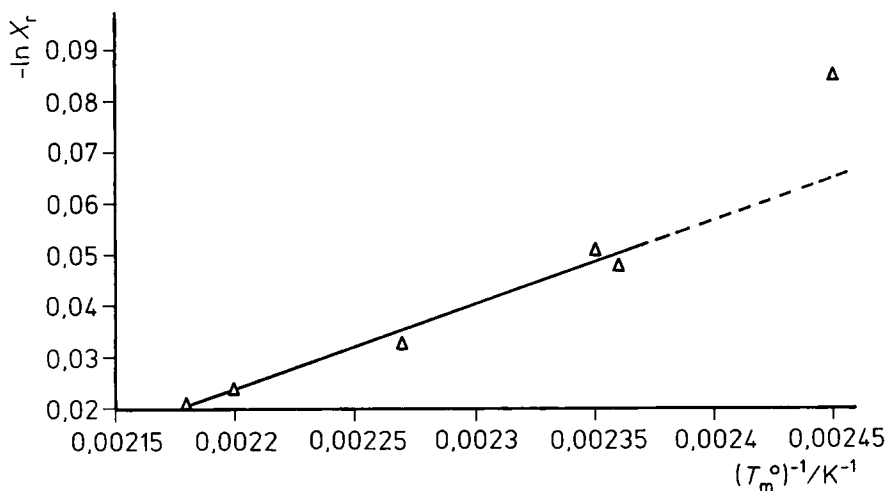


Fig. 4. Plot of $-\ln X_r$ vs $1/T_m^0$ according to the modified Flory equation (Eq. 2). The slope and the intercept of the least square lines fit to the points with the $(1/T_m^0 = 0)$ axis provide the values of $(T_m^0)_{100\%}$ ($= 487$ K) and ΔH_u ($= 1,4$ kJ/mol)

This is in agreement with a general trend observed for other stereoregular polymers as poly(1,2-butadiene) and polystyrene²⁹⁾.

Considering for the annealed sample 3 the fusion enthalpy (3,6 kJ/mol), obtained by differential calorimetry, and the crystallinity (51,8%), estimated by X-ray analysis²²⁾, a value of 6,9 kJ/mol can be calculated for the fusion enthalpy of the fully crystalline sample. In the literature there is a great uncertainty about the value of enthalpy of fusion reported for sPP⁸⁻¹²⁾ with values ranging from 1,9 kJ/mol to 3,1 kJ/mol. Recently¹⁷⁾ a value of 4,2 kJ/mol was reported for a highly sPP obtained with the Ewen's catalyst. The published values of ΔH_u for iPP range from 8,8 to 10,0 kJ/mol, thus being significantly higher than those observed for sPP. This is in contrast to what is reported for polystyrene³⁰⁾. In this case, the values of ΔH_u estimated for the isotactic and syndiotactic stereoisomers are comparable. Considering all these results, ΔH_u obtained from the Flory equation appears to be considerably low. This might lead to the conclusion that a right heat of fusion value for the syndiotactic polypropene cannot be properly estimated from our data by using the Flory equation. Work to confirm this hypothesis is in preparation.

Experimental part

Synthesis of syndiotactic polypropene (sPP) samples

General remarks

All manipulations of air-sensitive compounds were carried out under dry nitrogen atmosphere using the Schlenk-tube technique.

Polymerization reactions: The experiments 1–4 were performed in a Büchi glass autoclave (0,3, 2, 2 and 1 L, respectively) equipped with jacket, mechanical stirrer, manometer and capillar thermometer. The experiments 5 and 6 were carried out in a 100 mL glass autoclave equipped with magnetical stirrer, manometer and capillar thermometer. The autoclaves were washed before use with a solution of $\text{Al}(\text{CH}_3)_3$ in hexane.

Materials

The solvents used for the polymerization were distilled as follows: Toluene over $\text{TiCl}_4/\text{Al}(i\text{-C}_4\text{H}_9)_3$ and pentane over LiAlH_4 . The other solvents were purified according to standard procedures.

Methylaluminoxanes (MAO): The sample used in experiment 3 was synthesized according to Kaminsky³¹. In the other experiments the toluene Shering solution (ca. 14,6 wt.-% of Al and a molar mass of 800 g/mol) was employed.

Isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride was synthesized according to Ewen¹⁵ and characterized by ^1H NMR.

Polymerizations

Experiment 3 is reported as example: A solution of 559 mg of MAO in 720 mL of toluene was introduced into the autoclave and thermostated at 60 °C under 6 bar of propene pressure. A solution of 4,1 mg of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and 573,2 mg of MAO in 30 mL of toluene was then injected. The reaction was stopped after 6 h by injecting of 5 mL of methanol. The polymer was recovered by precipitation in methanol/HCl and further purified by extraction with boiling toluene. All sPP samples were found completely soluble.

Fractionation of sPP

Sample 3 was fractionated as usual³², by using Kumagawa extractors. The solvents used were the following: Hexane, heptane (at 213, 410, 760 Torr) and toluene.

Characterization methods

The inherent viscosity of the samples was measured in a 0,25 wt.-% solution of tetraline at 408 K.

Gel-permeation chromatography was carried out by using a Waters 150-C GPC equipped with Progel TSK columns, working at 408 K with 1,2-dichlorobenzene as solvent. Monodisperse fractions of polystyrene were used as standard.

^{13}C NMR spectra were recorded on a Bruker AM 300, at 393 K in deuterated tetrachloroethane. The resolution of the ^{13}C NMR spectra of syndiotactic polypropenes was digitally enhanced by convolution of the FID with a gaussian window function. The calculation of the pentads distribution was carried out according to the reported literature¹⁶.

The crystallization and melting behaviour were studied by differential calorimetry. A Perkin-Elmer DSC-7 calibrated with indium and tin standards was used. Weighed samples (3–5 mg) were sealed in an aluminium pan, heated until complete melting (443 K), kept at this temperature for two minutes and subsequently cooled with a nominal rate of 200 K/min at a fixed crystallization temperature (T_c). The heat released during the isothermal crystallization was recorded as a function of time and the fraction of crystallized material X was evaluated as the ratio of the heat evolved at time t over the total heat evolved. The $t = 0$ point was taken as the deflection point of the exotherms from the baseline after reaching the thermal equilibrium at T_c . The melting temperatures of the isothermally crystallized samples were determined by reheating directly from T_c at 10 K/min after the completion of the crystallization and were taken at the maximum of the endothermic peak. The heating rate of 10 K/min was chosen as the best compromise to avoid

recrystallization and superheating phenomena^{33,34}), as confirmed by a further work now in progress³⁵).

The isothermal crystallization experiments were performed starting from different temperatures in the melt phase in order to check the conditions where incompletely melted crystallites, that strongly influence the crystallization rate, were absent.

We are in debt to Prof. *Gianotti* for the stimulating discussions and the helpful suggestions. We would like to acknowledge *S. Bossi* and *T. Vercellio* for their technical assistance.

- 1) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti G. Masophio, *J. Am. Chem. Soc.* **77**, 1708 (1955)
- 2) EP 45977 (1981), Invs.: S. Parodi, R. Nocci, U. Giannini, P. C. Barbè, U. Scatà; Chem. Abstr. **96**, 181808w (1981)
- 3) V. Vittoria, "Properties of isotactic polypropylene" in Handbook of Polymer Science and Technology, ed. by M. Dekker, New York 1989, vol. 2, p. 507
- 4) R. B. Lieberman, P. C. Barbè, "Propylene Polymers" in Encyclopedia of Polymer Science and Engineering, J. Wiley & Sons, New York 1988, vol. 13, p. 4643
- 5) S. Van der Ven, "Polypropylene and other polyolefins", Elsevier, Amsterdam 1990
- 6) G. Natta, P. Pasquon, A. Zambelli, *J. Am. Chem. Soc.* **84**, 1488 (1962)
- 7) A. Zambelli, P. Locatelli, A. Rovasoli, D. R. Ferro, *Macromolecules* **13**, 267 (1980)
- 8) E. A. Youngman, J. Boor Jr., *Macromol. Rev.* **2**, 33 (1967)
- 9) D. R. Gee, T. P. Melia, *Polymer* **10**, 239 (1969)
- 10) A. Marchetti, E. Martuscelli, *J. Polym. Sci., Polym. Phys. Ed.* **12**, 1649 (1974)
- 11) U. Gaur, B. Wunderlich, *J. Phys. Chem. Ref. Data* **10**, 1051 (1981)
- 12) R. L. Miller, E. G. Seeley, *J. Polym. Sci., Polym. Phys. Ed.* **20**, 2297 (1982)
- 13) B. Lotz, A. J. Lovinger, R. E. Cais, *Macromolecules* **21**, 2375 (1988)
- 14) A. J. Lovinger, B. Lotz, D. D. Davis, *Polymer* **31**, 2253 (1990)
- 15) J. A. Ewen, R. J. Jones, A. Razavi, J. D. Ferrara, *J. Am. Chem. Soc.* **110**, 6255 (1988)
- 16) A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, *Macromolecules* **21**, 617 (1988)
- 17) A. Galambos, M. Wolkowicz, R. Zeigler, M. Galimberti, *Polym. Prep. A.S.C. Polymer Materials Science and Engineering Div.*, **45** (1991)
- 18) T. Tsutsui, A. Mizuno, N. Kashiwa, *Makromol. Chem.* **190**, 1177 (1989)
- 19) Y. P. Khanna, T. J. Taylor, *Polym. Eng. Sci.* **28**, 1042 (1988)
- 20) D. R. Norton, A. Keller, *Polymer* **26**, 704 (1985)
- 21) L. Mandelkern, "Crystallization of Polymers", Mc Graw-Hill, 1964, p. 33
- 22) M. Galimberti, D. Dainelli, G. Balbontin, G. Paganetto, in preparation
- 23) J. D. Hoffmann, J. J. Weeks, *J. Res. Nat. Bur. Stand., Sect. A* **66**, 13 (1962)
- 24) See ref.²¹), p. 33
- 25) S. Z. D. Cheng, J. J. Janimak, A. Zhang, H. N. Cheng, *Macromolecules* **23**, 298 (1990)
- 26) P. J. Flory, *Trans. Faraday Soc.* **390**, 51 (1955)
- 27) R. L. Miller, L. E. Nielsen, *J. Polym. Sci.* **46**, 303 (1960)
- 28) R. L. Miller, *J. Polym. Sci.* **57**, 975 (1962)
- 29) *Polymer Handbook*, ed. by J. Brandrup, E. H. Immergut, Wiley and Sons Publishers, New York, 2nd ed., 1975
- 30) G. Gianotti, A. Valvassori, *Polymer* **31**, 473 (1990)
- 31) DE 3,240,383 (1982), Invs.: W. Kaminsky, H. Hansen; Chem. Abstr. **101**, P73242n (1982)
- 32) G. Natta, P. Pino, G. Mazzanti, *Gazz. Chim. Ital.* **87**, 528 (1957)
- 33) E. Hellmuth, B. Wunderlich, *J. Appl. Phys.* **36**, 3039 (1965)
- 34) V. Petraccone, G. Guerra, C. De Rosa, A. Tuzi, *Macromolecules* **18**, 813 (1985)
- 35) G. Balbontin, M. Galimberti, T. Vercellio, in preparation