Crystallization behaviour of fractions of isotactic polypropylene with different degrees of stereoregularity

E. Martuscelli, M. Pracella and L. Crispino
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR – ARCO Felice Napoli, Italy
(*Received* 27 *July* 1982)

The influence of the degree of stereoregularity on the overall rate of crystallization and on the melting behaviour of fractions of isotactic polypropylene has been investigated. Fractions with different stereoregularity were obtained by extraction methods. The stereochemical pentad population was determined by ^{13}C n.m.r. analysis. The results show that at constant T_c the overall rate constant of crystallization decreases with the increase of configurational chain defects whereas at a given ΔT the contrary is observed. An evident phenomenon of secondary crystallization is observed only in fractions of IPP with a higher concentration of defects. Such observation may explain the double peaked endotherm of fusion of more defective IPP fractions. The free energy of formation of a nucleus of critical dimensions has been calculated for each fraction and its value correlated with the degree of stereoregularity.

Keywords Isotactic polypropylene; stereoregularity; crystallization; thermal behaviour

INTRODUCTION

The presence of configurational defects in isotactic polypropylene (IPP) chains influences the morphological characteristics, the thermal behaviour, the rheological and mechanical properties of this polymer.

A deeper knowledge of the relation between property and structure of the IPP is limited to the possibility of obtaining detailed information on its microstructure. The use of nuclear magnetic resonance (^{13}C n.m.r.) allows an accurate estimate of the fractions of isotactic, syndiotactic and atactic pentads and the distribution of irregularly arranged (head to head) units in the IPP chains[1].

In a previous work the influence of the stereoregularity degree of IPP fractions, characterized by ^{13}C n.m.r. on the morphology and on the melting and annealing behaviour of solution grown single crystals was examined[2]. It has been found that the structural regularity of the crystals, the dissolution and melting temperatures, notably decrease when the fraction of isotactic pentads in the samples decrease.

The purpose of the present work is to investigate the kinetics of crystallization from melt of IPP fractions with different degrees of stereoregularity in order to examine the influence of the stereochemical composition of the samples on the kinetic and thermodynamic parameters which control the crystallization process.

In particular this work aims at deepening the effect of the concentration and of the distribution of the uncrystallizable units (syndiotactic and atactic pentads) on:

(a) kinetics of primary and secondary crystallization;

(b) values of the free energy of formation of a nucleus of critical dimensions and of the surface free energy of the crystals;

(c) melting behaviour of the IPP crystals.

EXPERIMENTAL

Materials

Three different fractions of isotactic polypropylene were examined. Two of these fractions (samples T96 and T64) were obtained by propene polymerization with the catalyst system $\mathscr{S}$–TiCl$_3$ (HRA Stauffer) and Al–(C$_2$H$_5$)$_2$Cl in toluene at 76°C in a rocking stainless-steel autoclave. The third fraction (sample V85) was prepared by using the catalyst system VCl$_3$ and Al(C$_2$H$_5$)$_3$ at 15°C.

The polymerization techniques and the purification of the products from the catalysts are described in detail elsewhere[3].

Fractions of varying stereoregularity were obtained by successive extractions with hydrocarbon solvents or by isothermal fractional crystallization[4]. Intrinsic viscosity measurements in tetrahydronaphthalene at 135°C show

0032–2861/83/060693–07$3.00

Table 1 Stereochemical composition (mole fraction) of isotactic polypropylene fractions

Sample	Isotactic pentads (%)^a			Syndiotactic pentads (%)^a			Atactic pentads (%)^{a}mmrm			$-\!(CH_2)\!-^b$ (g/100 g)
	mmmm	mmmr	rmmr	rrrr	mrrr	mrrm	mmrr	rrmr	mrmr	
T96	95.8	1.7	0	0	0	0.8	1.7	0	0	<0.5
T64	63.9	6.7	1.2	6.4	2.0	5.1	8.3	6.0	0.6	0.4
V85	84.6	3.9	1.2	0.4	1.2	1.7	5.1	1.8	0	<0.5

[a] Determined by ^{13}C n.m.r. analysis (see text)

[b] Amount of head-to-head chain irregularities (in g) of $-(CH_2-CH_2)-$ units per 100 g of polymer

each sequence $-CH(CH_3)CH_2CH_2CH(CH_3)-$ denotes one error in the arrangement of the monomer units

that all the fractions were of sufficiently high molecular weight to suggest that chain regularity rather than molecular weight played the dominant role in the fractionation[4]. The stereochemical pentad population of each fraction was determined by ^{13}C n.m.r. analysis[1]. The mole fractions of the different types of pentads are reported in *Table 1*.

Calorimetric measurements

All the measurements were carried out with a Perkin-Elmer DSC-2 differential scanning calorimeter operating under N_2 atmosphere. Polymer samples weighing 10 mg (about) closed in aluminium pans, were used throughout the experiments. The d.s.c. temperature scale was calibrated using the melting temperature of high purity standards.

The kinetics of isothermal crystallization from melt of various fractions was studied by employing the following procedure: samples were kept for 10 min at a temperature ~30 K higher than their melting point and then rapidly cooled (320 K min^{-1}) to the crystallization temperature T_c. The heat (dH/dt) evolved during the isothermal crystallization was recorded as a function of time and the fraction X_t of material crystallized after the time t was calculated from the relation:

$$X_t = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt$$

where the first integral is the crystallization heat generated at the time t and the second integral is the total crystallization heat for $t = \infty$.

Melting endotherms of the samples after crystallization at T_c were recorded by heating the samples directly from T_c to the observed melting point T_m' with heating rates of 20 and 80 K min^{-1}. The melting temperature T_m' and the apparent enthalpy of fusion ΔH_f^* were measured at the maxima and from the area of the melting endotherms respectively.

RESULTS AND DISCUSSIONS

Crystallization behaviour

The kinetics of crystallization from the melt of the three fractions of isotactic polypropylene have been studied in the temperature interval 378–404 K.

Figure 1 illustrates the crystallization isotherms at various T_c of the fractions T96 and T64. The variation of the half time of crystallization $t_{0.5}$ with T_c and with the undercooling ΔT, defined as the difference between the equilibrium melting temperature T_m and T_c, is shown in *Figures 2* and *3* respectively.

From the trend of the curves it emerges that sample T64, has values of the overall rate constant of crystallization that are lower than those of sample T96 (higher values of $t_{0.5}$) at the same T_c; whereas at the same ΔT, they are higher.

It is also interesting to observe that increasing the stereoregularity degree of the fraction, the value of T_c must be increased in order to keep the same rate of crystallization. This observation is of practical interest; in fact for a given rate of crystallization it is possible to

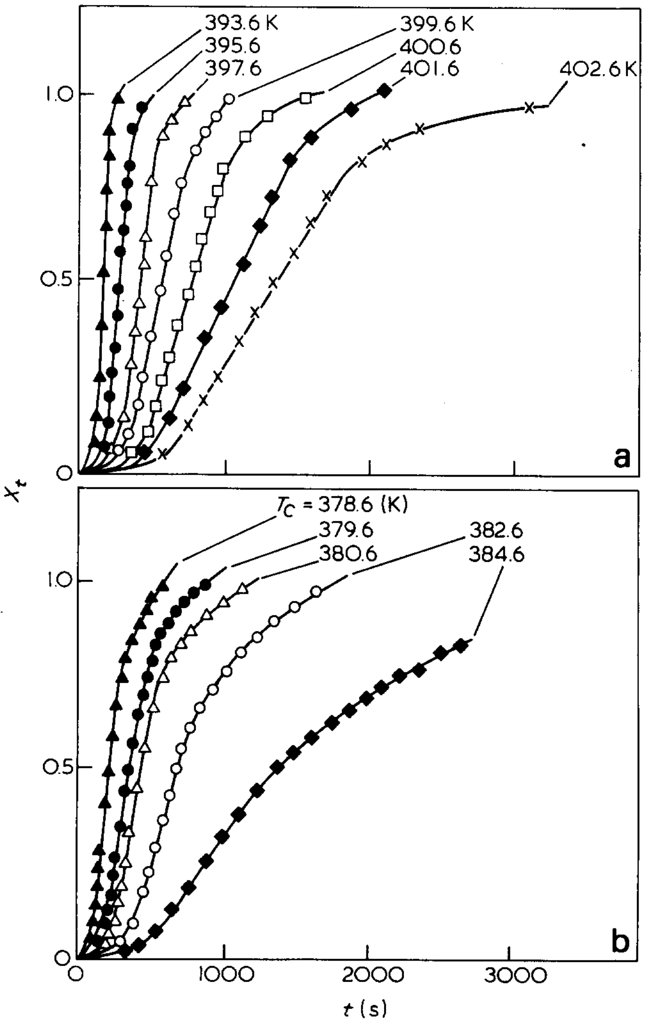

Figure 1 Typical crystallization isotherms of isotactic polypropylene fractions at various crystallization temperatures T_c: (a) Fraction T96; (b) Fraction T64

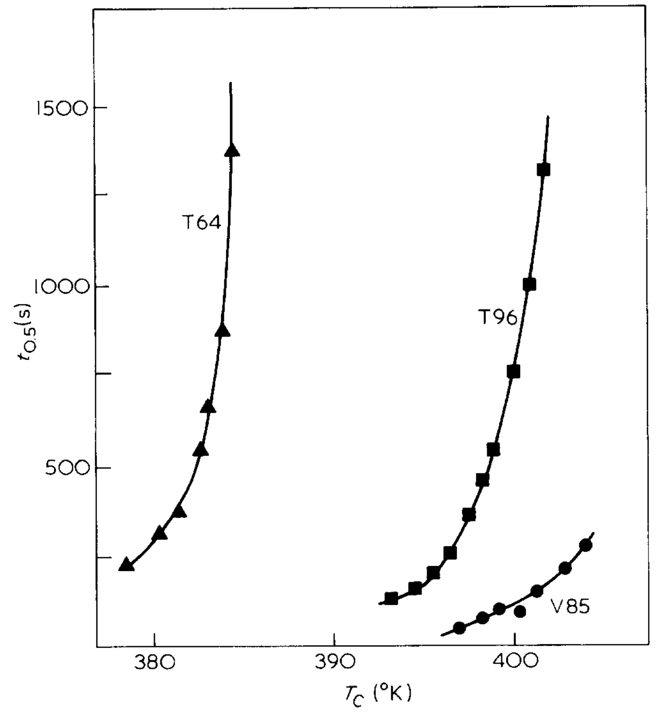

Figure 2 Half time of crystallization $T_{0.5}$ of IPP fractions as function of crystallization temperature T_c

crystallize the isotactic polyproylene at lower T_c simply by decreasing the degree of tacticity (the T64 fraction, 64% of mmmm pentads, crystallizes at T_c which is ~17 degrees lower than those corresponding to the fraction having 96% pentads mmmm).

As can be observed in *Figures 2* and *3* fraction V85 behaves in an anomalous way. In fact although this fraction has a concentration of isotactic pentads that is in intermediate between that of fraction T96 and T64 it has a higher crystallization rate both at the same T_c and at the same ΔT.

This behaviour may be attributed to the fact that for fractions prepared by using vanadium based catalyst, nucleant effects due to impurities are present. The distribution of the stereoirregularities along the macromolecules of such fraction could also account for this anomalous behaviour.

In a previous work we investigated the influence of chain irregularities, chemical defects and counits, randomly distributed along the macromolecules, on the kinetics of crystallization of several polymeric systems such as ethylene–butadiene[5] and isotactic propylene–butene-1 random copolymers[6].

In both cases it has been observed that the overall rate constant of crystallization at a given T_c, decreases with the increase of butene-1 and butadiene units along the chains of IPP and polyethylene respectively. In these copolymers, such units act as chemical defects of the constitutional type.

The results of the present investigation together with those obtained in the case of the above mentioned copolymers lead to the conclusion that the overall kinetics of crystallization of polymers is strongly influenced and controlled by the concentration and distribution of chemical defects that are present along the chains.

Keith and Padden, analysing the radial growth rate of polypropylene spherulites in mixtures of isotactic polymer (extracted and non-extracted) with atactic polymer with various molecular weights, found that under the same undercooling the spherulites grew faster the higher the concentration of the diluent atactic polymer (see *Table 2*).

Furthermore the spherulites of IPP which were not extracted showed a growth rate nearly twice as high as the extracted IPP. They attributed this behaviour to the 'impurities' present (stereoirregular molecules and fractions with low molecular weight) which tent to speed up the transport processes in the melt.

It is important to emphasize the fact that the influence of the stereoirregularity of the molecules on the crystallization kinetics of the IPP may be considered analogous when stereoirregular sequences are 'incorporated' in the chains and when these sequences are 'added' under the form of atactic molecules.

It is likely that in the case of incorporation along the chain of defective units, it is the flexibility of the chains rather than the transport process phenomena that is mainly responsible for the observed behaviour.

The analysis of the kinetics of crystallization of the fractions of IPP, for each T_c, has been carried out on the basis of Avrami's equation[8]:

$$(1-X_t)=\exp[-K_n t^n] \qquad (1)$$

where X_t is the polymer fraction which is crystallized at time t, k_n is the overall kinetic rate constant and n is a

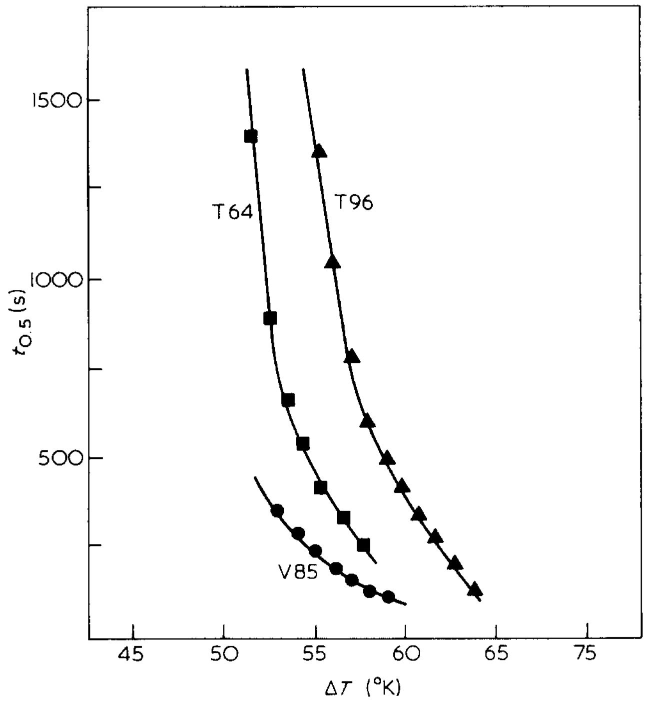

Figure 3 Half time of crystallization $t_{0.5}$ of IPP fractions as function of undercooling ΔT

---

* It must be pointed out that fractions of IPP obtained by using vanadium based catalysts have a molecular weight that is higher than those of fractions obtained by using titanium based catalysts. The rate of dissolution of these polymers was very low. As a consequence the distribution of the stereochemical composition of the macromolecules in each fraction was rather broad. The corresponding average stereoisomeric composition (determined by n.m.r.) is noticeably different from that of the more stereoisomerically pure macromoledules of the fraction. On the other hand it must be noted that dissolution and melting temperatures refer to the more sterically pure material[2].

Table 2 Spherulite growth rates at different undercoolings $\Delta T = T'_m - T_c$ for blends of unextracted isotactic polypropylene (IPP) with atactic polypropylene (APP) for various compositions (Data by H. D. Keith and F. J. Padden[7])

Sample IPP/APP	Radial growth rates (μ/min) $\Delta T = 51$	$\Delta T = 40$	$\Delta T = 36$	Melting point (°C)
100/0	29.4	3.9	1.6	171
80/20	50	8	3	167
60/40	100	15	8	165

Note: The values of the undercooling in the Table are much lower than those reported by us in *Fig 3* even though the crystallization temperatures investigated are in the same range ($105 < T_c < 130°$). The reason for this discrepancy is probably due to the fact that the undercooling values in Ref.7 have been determined using the observed melting point of the samples which are lower than the respective equilibrium values.

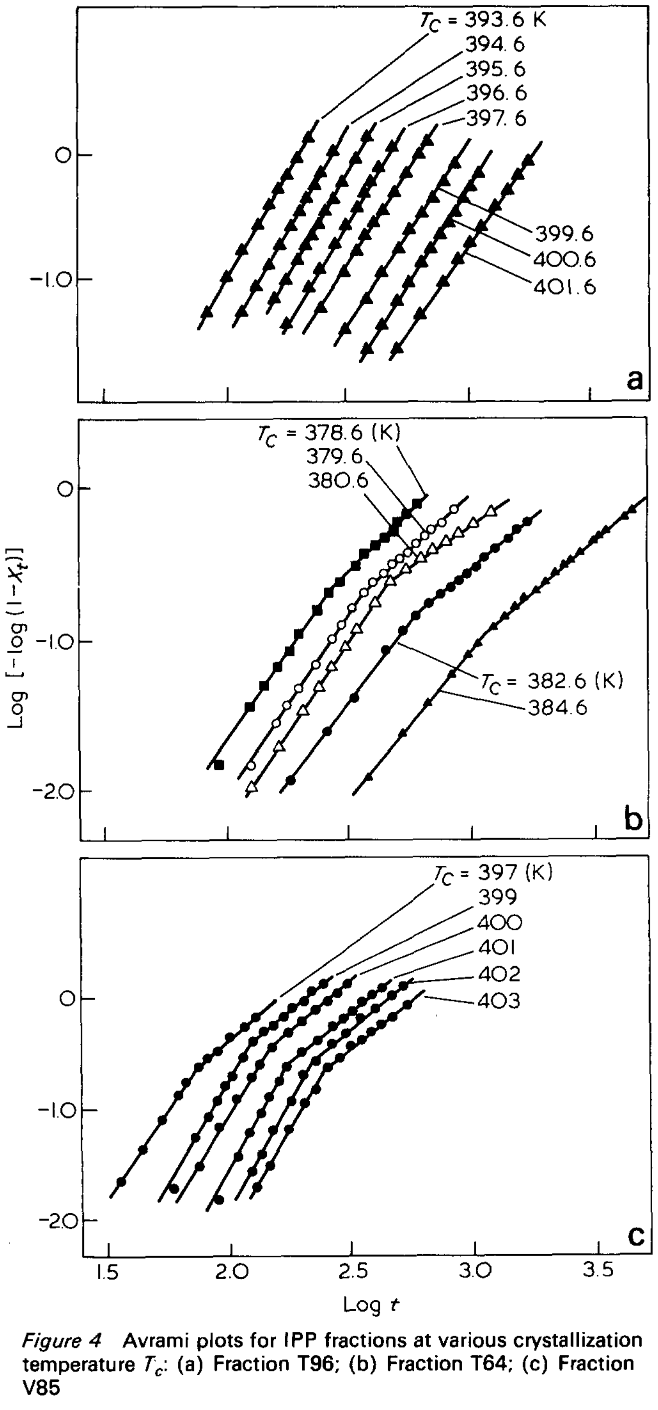

Figure 4 Avrami plots for IPP fractions at various crystallization temperature T_c: (a) Fraction T96; (b) Fraction T64; (c) Fraction V85

parameter that is dependent from the nucleation process and from the geometry of growth of the crystals.

In *Figure 4*, the quantity log $[-\log(1-X_t)]$ is reported against log t, for the three samples examined and for each T_c investigated.

As shown in *Figure 4a*, Avrami's plots of fraction T96 at different T_c show a linear trend with no change in the slope up to a high degree of conversion. On the contrary the plots of fraction V85 and T64 (*Figures 4b* and *c*) present, at a certain time and degree of conversion, a sharp slope variation. This is verified in all cases for values of X_t going from 50% to 30%.

The values of k_n and n determined respectively by the intercepts and slopes of the straight lines of *Figure 4* are reported in *Table 3*.

For samples T64 and V85 two sets of values have been derived for k_n and n corresponding to the two linear parts of the plots having different slopes. Values of K_n have been calculated also by using the relation:

$$k_n = \log_e 2/t^n_{0.5}$$

In the regions with higher slopes samples V85 and T64 have average values of n of 3 and 2.7 respectively, whereas for longer conversion times these values are reduced to 1.6 and 1.7. For sample T96 n assumes an average value of 3.1 (see *Table 3*).

In accordance with literature[9] the trend observed in the plots of *Figures 4b* and *c* and the variation of the coefficient of Avrami found for sample V85 and V64 is explained by the existence of primary and secondary crystallization processes in the material.

According to the theory, n should be a combined function of the number of dimensions in which growth takes place and also of the order of the time dependence of

Table 3 Avrami exponent n, half time of crystallization $t_{0.5}$; $-\log_{10} K_n$ as function of the crystallization temperature T_c for IPP fractions. The equilibrium melting temperature T_m is also reported

Sample	T_c (K)	$t_{0.5}$ (s)	$-\log_{10} K_n$	n	n'	T_m (K)
T96	393.6	130	6.48	3.4		(458)
	394.6	175	6.87	3.5		
	395.6	230	7.23	3.4		
	396.6	295	7.56	3.3		
	397.6	380	7.89	3.0		
	398.6	460	8.16	2.9		
	399.6	550	8.37	3.0		
	400.6	750	8.79	2.9		
	401.6	1010	9.18	2.7		
	402.6	1300	9.51	2.7		
T64	378.6	236	6.60	2.9	1.8	(436)
	379.6	322	6.99	2.9	1.9	
	380.6	368	7.14	2.9	1.5	
	381.6	561	7.65	2.8	1.7	
	382.6	618	7.74	2.6	1.8	
	383.6	891	8.19	2.4	–	
	384.6	1312	8.64	2.5	1.7	
V85	397	81	6.65	3.4	1.6	(456)
	398	110	7.10	3.6	1.5	
	399	129	7.34	3.4	1.6	
	400	144	7.50	3.6	1.6	
	401	207	8.03	3.3	1.5	
	402	258	8.36	3.4	1.5	
	403	308	8.62	3.3	1.6	

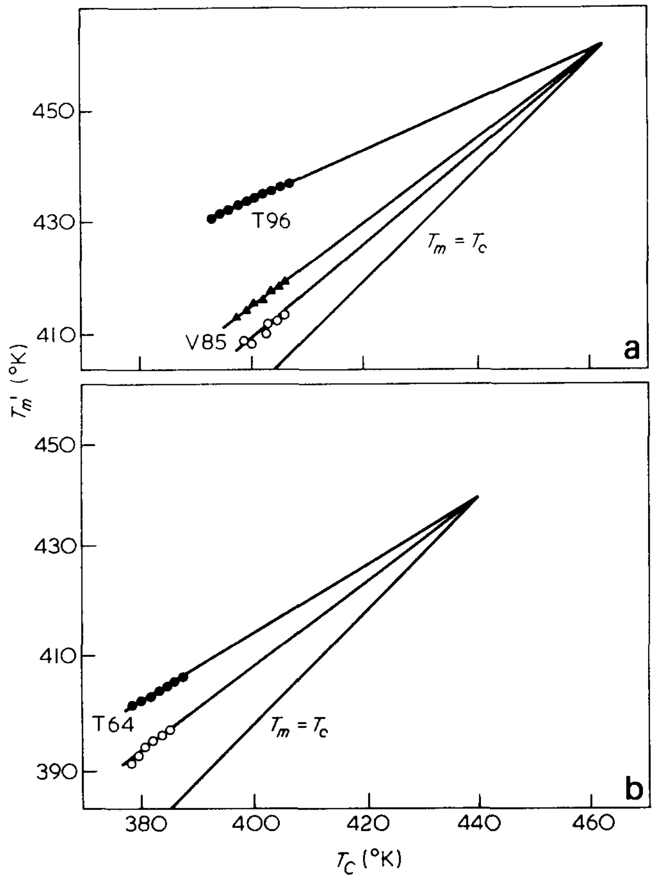

Figure 5 Variation of the observed melting temperature T'_m with T_c: (a) Fraction T96 and V85; (b) Fraction T64

the nucleation process. Accordingly *n* should assume a value of 4 when three dimensional spherulitic growth units develop from nuclei whose concentration increases linearly with time.

In the case of IPP fractions and in the first stage of crystallization (primary crystallization) *n* has almost the same value of about 3 irrespective of defect concentration. Such observations indicate that the mechanism of primary nucleation and of growth for low times of crystallization is probably the same for the three fractions investigated (spherulitic growth from instantaneous nuclei).

For samples T64 and V85 in the second stage (secondary crystallization) the crystallization proceeds at a lower rate according to an Avrami type law with n' that is between 1 and 2. These values of *n* are characteristic of a crystallization process with a one dimensional growth habit, linear growth and heterogeneous nucleation[10-12].

Hoshino *et al.*[13], studying the kinetics of isothermal crystallization of polypropylene, have shown that their results could be interpreted on the basis of a two stage model of crystallization characterized by a primary crystallization with $n = 3.9$ and a secondary crystallization process with $n' = 1.8$.

According to literature[10-12] a process of secondary crystallization may result from the crystallization of a more difficult crystallizable component and/or from an increase in the perfection of the existing crystallites following an annealing at T_c.

The finding that only IPP fractions with less degree of stereoregularity present an evident secondary crystallization which strongly suggests that this process in the case of isotactic polypropy.ene is mainly due to the crystallization of the less perfect IPP molecules in interlamellar regions.

These conclusion are in agreement with the morphological observations on solution grown crystals of IPP fractions. As reported by us in a previous paper crystals with a regular and simple morphology are obtained only from fractions of IPP with higher degrees of stereoregularity[2].

With fractions having a larger concentration of defects it is very difficult to find crystallization conditions leading to monolayer single crystals with a simple morphology. Very complicated and ill-defined multilayer crystals are more often observed[2].

Melting behaviour

The melting behaviour of the IPP fractions is notably influenced by the degree of stereoregularity. In fact d.s.c. thermograms of V85 and T64 fractions (registered at a heating rate of 20°C min^{-1}) show for all the crystallization temperatures a double melting peak, in analogy with that already found in the case of crystals of the same fractions grown from diluted solutions[2].

On the contrary the thermograms of fraction T96 always present a single fusion peak. *Figure 5* reports the trend of the observed melting temperatures T'_m as function of T_c for T96, V85 and T64 samples.

In all cases a linear increase of T'_m when T_c increases is observed in accordance with relation[14]

$$T'_m = \left[\frac{\gamma - 1}{\gamma}\right] \cdot T_m - \frac{1}{\gamma} T_c \qquad (2)$$

where γ is a constant and T_m is the equilibrium melting temperature. The value of T_m, for each sample, is determined by the intersection point of the straight line of equation (2) with the straight line $T'_m = T_c$. The equations of the straight lines obtained by plotting T'_m *versus* T_c, obtained by least-squares method, are reported in *Table 4* together with the extrapolated values of T_m.

For the sample T96, with the highest fraction of isotactic pentads, T_m is equal to 458 K. This value agrees quite well with values reported by Godovsky *et al.*[15] (458 K), Ullmann *et al.*[16] (459 K) and by Wunderlich[17] (460.5 K) determined isothermally on samples of isotactic polypropylene crystallized from the melt.

A value for T_m, slightly lower (451 K) was found in the case of solution grown crystals of T96 fraction[2].

In the cases of samples V85 the temperature of the two melting peaks show, when plotted *versus* T_c, an almost parallel trend and extrapolate to different values of T_m namely 456 K and 440 K respectively.

For the T64 sample the temperature of the double peaks both seem to extrapolate at the same T_m (436 K).

Table 4 Equations of the straight line $T'_m - T_c$ (see *Figures 5a* and *b*. The values of T_m are also reported

Sample	Eq.(2)	T_m (K)
T96	$T'_m = 278.6 + 0.390T_c$	458
V85	$^aT'_m = 122.4 + 0.731T_c$	456
T64	$^aT'_m = 176.8 + 0.593T_c$	436

[a] from the higher temperature peak

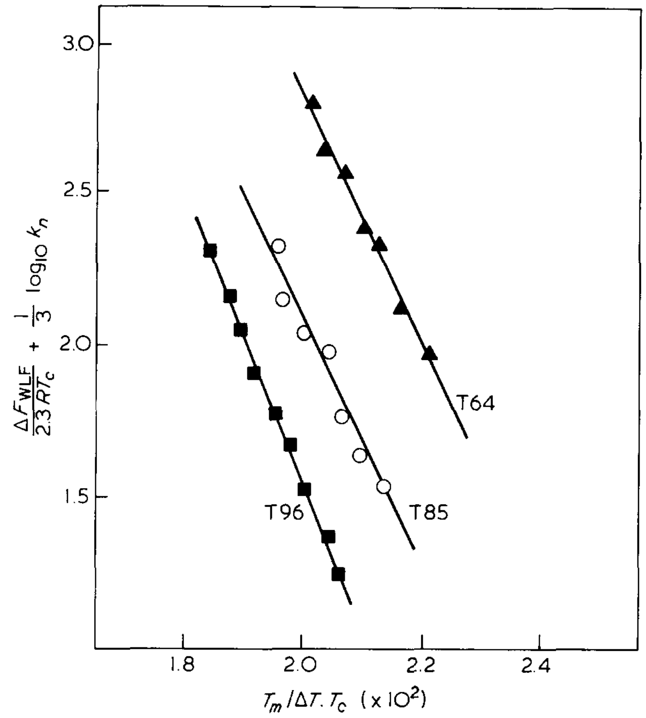

Figure 6 Plot of (1/3) $\log^{10} K_n + \Delta F_{WLF}/(2.3RT_c)$ against $T_m/(T_c\Delta T)$ for IPP fractions

Multiple endotherms of fusion were also observed by us in the d.s.c. thermograms of solution grown crystals of the same IPP fractions (V85 and T64).

A detailed analysis of the phenomenon led us to the conclusion that the two melting peaks most likely correspond to the fusion of crystalline regions with an different average degree of order[2]. In other words it was suggested that, when polymers with configurational chain defects are allowed to crystallize isothermally at rather low undercooling, segments of higher stereoregularity prefer to pack into more perfect crystalline regions.

In the light of the kinetic observations more may be said about the origin and nature of the double peaked fusion of IPP. The two melting peaks observed in fractions of IPP with less degree of stereoregularity may be related to the existence of processes of primary and secondary crystallization in the samples. Accordingly the higher melting temperature should correspond to the fusion of lamellar crystals formed during the process of primary crystallization whereas the lower one corresponds to the fusion of crystals grown mainly in interfibrillar regions, during the secondary crystallization process.

It is interesting to observe that fraction V85, even having a value of T_m, extrapolated from the highest temperature peak, almost coincident with that of fraction T96, presents a value of the slope of the straight line $T'_m - T_c$ higher than that of sample T96.

According to equation (2) this means, a lower value of the γ parameter (as a matter of fact we found: γ(T96) = 2.56 and γ(V85) = 1.37). According to the kinetic theories of polymer crystallization γ is determined by the ratio between the final L and initial L^* thickness of the growing lamellae.

Our results indicate that the process of isothermal lamellar thickening at T_c is more difficult for polypropylene having a higher defect content and/or a higher molecular weight. Thus it may be concluded that small differences in the stereoregularity of the samples influence not only the melting behaviour but also the annealing behaviour of IPP crystals.

Temperature dependence of the overall kinetic rate constant

Assuming that for the IPP fractions the process of crystal growth corresponding to the primary crystallization is controlled by a mechanism of surface coherent bidimensional nucleation, then in accordance with the kinetic theory of polymer crystallization[14,18] the temperature dependence of the overall kinetic rate constant may be expressed with the relation:

$$\frac{1}{n}\log K_n = A_0 - \frac{\Delta F^*}{2.3RT_c} - \frac{\Delta\Phi^*}{2.3KT_c} \qquad (3)$$

where ΔF^* is the activation energy for the transport of the molecules from the liquid to the solid interface; A_0 is a constant (in the hypothesis that the density of primary nucleation at the T_c examined does not vary with time) and $\Delta\Phi^*$ is the energy of formation of a nucleus of critical dimensions expressed as:

$$\Delta\Phi^* = \frac{4b_0\sigma\sigma_e T_m}{\Delta H_F \Delta T} \qquad (4)$$

In equation (4) b_0 is the distance between two adjacent fold planes, σ and σ_e are the free energy of formation per unit area of the lateral and folding surfaces of the crystals and ΔH_F is the enthalpy of fusion. The transport term ΔF^* is usually expressed as the activation energy of the viscous flow according to the relation of William Landel and Ferry[19]:

$$\Delta F^* = \Delta_{WLF} = C_1T_c/(C_2 + T_c - T_g) \qquad (5)$$

where C_1 and C_2 are constants generally assumed equal to 4.12 kcal mol^{-1} and 51.5 K respectively and T_g is the glass transition temperature. For all the samples examined $T_g = 249$ K has been used, that is to say the T_g of the isotactic polypropylene reported in literature[20].

For all samples investigated, as shown in *Figure 6*, plots of $\frac{1}{3}(\log_{10}K_n) + \Delta F//(2.3RT_c)$ against $T_m/(T_c\Delta T)$ are straight lines (for n an average value of 3 was used throughout). The slopes of this line according to equation (3), give the values of the quantity:

$$-4b_0\sigma\sigma_e/(2.3K\Delta H_F) \qquad (6)$$

By using equation (4) the free energy of formation of a nucleus of critical dimensions $\Delta\Phi^*$, may be easily calculated at any ΔT. The values are reported in *Table 5*. As can be seen $\Delta\Phi^*$ at a given ΔT seems to increase with the increase of the stereoregularity of the IPP fractions.

Table 5 Free energy of formation of a nucleus of critical dimensions, for IPP fraction, as function of ΔT

Sample	(kcal/mol) ΔT = 50 K	ΔT = 55 K	ΔT = 60 K
T96	19	17	16
V85	17	15	14
T64	16	15	14

It is interesting to underline that a similar trend in $\Delta\Phi^*$ was observed by us in the case of isotactic propylene–butene-1 random copolymers crystallizing in the IPP phase (low butene content region). In such a case $\Delta\Phi^*$ was found to decrease with the increase of the butene-1 concentration[20].

The finding that $\Delta\Phi^*$ at constant ΔT decreases with the increase of the defect content in IPP fractions is in agreement with the experimental trend observed in the plot $t_{0.5} \rightarrow \Delta T$ of *Figure 3* that is with the observation that at a given ΔT IPP fractions with higher degree of stereoregularity have higher values of $t_{0.5}$ (lower overall rate of crystallization).

ACKNOWLEDGEMENT

This work was supported partly by Progetto Finalizzato Chimica Fine del C.N.R.

REFERENCES

1 Zambelli, A., Locatelli, P., Brjo, G. and Bovey, F. A. *Macromolecules* 1975, **8**, 687; Zambelli, A. and Gatti, G. *ibid.* 1978, 485
2 Martuscelli, E., Pracella, M. and Zambelli, A. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 619
3 Natta, G., Pasquon, L., Zambelli, A. and Gatti, G. *J. Polym. Sci.* 1961, **51**, 387; Zambelli, A., Segre, A. L., Farina, M. and Natta, G. *Makromol. Chem.* 1967, **110**, 1
4 Pavan, A., Provasoli, A., Moraglio, G. and Zambelli, A. *Makromol. Chem.* 1977, **178**, 1099
5 Amelino, L. and Martuscelli, E. *Polymer* 1975, **16**, 864
6 Crispino, L., Martuscelli, E. and Pracella, M. *Makromol. Chem.* 1980, **181**, 747
7 Keith, H. D. and Padden, F. J. *J. Appl. Phys.* 1964, **35**, 1286
8 Avrami, M. *J. Chem. Phys.* 1939, **7**, 1103; 1940, **8**, 212
9 Wunderlich, B. 'Macromolecular Physics', Vol. 2, Academic Press, New York, 1976, p. 235
10 Sharples, A. 'Introduction to Polymer Crystallization', Publishers Ltd., London, 1966
11 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill (N.Y.), 1964
12 Zachmann, H. G. and Stuart, H. A. *Makromol. Chem.* 1960, **41**, 131
13 Hoshino, S., Meinecke, E., Powers, J., Stein, R. S. and Newmann, S. *J. Polym. Sci. Part A* 1965, **3**, 3041
14 Hoffmann, J. D. *SPE Trans.* 1964, **4**, 315
15 Godovsky, Yu K. and Slonimsky, G. L. *J. Polym. Sci. Polym. Phys. Edn.* 1974, **12**, 1053
16 Ullmann, W. and Wendorff, J. H. *Progr. Colloid Polym. Sci.* 1979, **66**, 25
17 Wunderlich, B. 'Macromolecular Physics, Crystal Melting', Vol. 3, Academic Press, New York, 1980, p. 63
18 Turmbull, D. and Fisher, J. C. *J. Chem. Phys.* 1949, **17**, 71
19 Williams, H. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
20 Crispino, L., Martuscelli, E. and Pracella, M. *Makromol. Chem.* 1980, **181**, 1747