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CRYSTALLIZATION KINETICS OF METALLOCENE TYPE POLYPROPYLENES
Influence of molecular weight and comparison with Ziegler-Natta type systems

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Abstract

The crystallization kinetics from the melt of metallocene type isotactic poly(propylenes) having the same chain defect concentration and molecular weights ranging from 68480 to 288430 have been studied by differential scanning calorimetry. The crystallization rates and the variation of the rates with crystallization temperature follow a pattern that is basically independent of molecular weight. This result contrasts with the molecular weight dependence on the crystallization rate observed in linear polyethylene, random ethylene copolymers as well as other semicrystalline systems.

Most significant is the fact that the metallocene poly(propylenes) show apparently significantly higher $\sigma_e\sigma_u$ products than do the Ziegler type fractions of matched molecular weight and defect concentration. This difference can be interpreted as the metallocene type crystallites having higher effect on surface interfacial free energies than the Ziegler type, or can result from the two different chain types having different sequence propagation probabilities.

Keywords: crystallization kinetics, metallocene type poly(propylenes)

Introduction

The crystallization kinetics from the melt of isotactic poly(propylenes), prepared with heterogeneous Ziegler-Natta type catalysts, have been extensively studied during the last two or three decades. Parameters such as molecular mass, molecular mass distribution and the stereoirregularity of the chains are known to influence the crystallization behavior as does the formation of the different known crystallographic forms and lamellar morphologies. In spite of the large number of papers related to this subject [1–16], there, however, have been

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very few works where direct efforts were made to analyze these variables independently from one to another [17, 18]. In order to carry out such studies it is necessary to use molecular weight fractions, or samples with narrow distributions, that have a constant chain defect concentration. The intrinsic heterogeneity of molecular weight and defect composition from chain to chain of the Ziegler-Natta type poly(propylenes) seriously hamper such studies. It is well established that in these types of polymers the highest molecular weight species contain the least number of defects and vice versa [19].

The new generation of homogeneous transition metal catalysts, the metallocenes, yields more homogeneous poly(propylenes) [20]. The molecular weight distribution is close to a most probable one and the defect distribution is narrow from chain to chain. The versatility of this new generation of catalysts allows for a better control of the type and concentration of defects. Thus, samples in which the molecular weight can be varied over a broad range while the same defect concentration is maintained are now available for analysis. The influence of the molecular weight on the crystallization kinetics, and on the temperature coefficient, can now be studied independent of the defect concentration. The present paper represents an initial study of the overall crystallization kinetics of a set of metallocene based isotactic poly(propylenes) that encompass a wide range in molecular weights, at a fixed chain defect concentration. In addition, the result of a comparative study of the crystallization kinetics between a molecular weight and composition fraction obtained from a conventional Ziegler-Natta supported type catalyst and a metallocene type poly(propylene) having similar molecular weights and defect concentration will be presented and discussed.

Emphasis will be given to the absolute crystallization rates, the temperature coefficient of the crystallization, the influence of nucleation and transport processes, and the type of Regimes that are observed.

Experimental

The metallocene-based poly(propylenes) that were used in this study are experimental polymers. Their characterizations are listed in Table 1. In one set the molecular masses range from 68480 to 288430 g mol^{-1}. The concentration of total chain defects is constant in this series. These polymers contain approximately 0.9 stereo-type defects per 100 total pentads and about 0.8 regio-type defects per 100 total carbons. The crystallization rates of two other poly(propylenes) were also studied. Their characteristics are also listed in Table 1. B-18 is a high molecular weight, low defect content fraction from a Ziegler-Natta type poly(propylene). Its fractionation and characterization have been reported previously [19, 21, 22]. Sample D-M is a metallocene type poly(propylene) with very similar molecular weight and the same total defect content as polymer B-18. This sample is a special Hoechst exclusive research product.

Table 1 Characterization of poly(propylenes)

Samples	M_W	M_W/M_N	Isotacticity[a]	Stereo defects	Regio[b] defects	Total defects
Metallocenes						
M-IPP 68K	68480	2.0	0.940	0.97	0.60	1.57
M-IPP 69K	69190	2.1	≈0.95	≈0.9	≈0.8	≈1.7
M-IPP 142K	142000[c]	–	≈0.95	≈0.9	≈0.8	≈1.7
M-IPP 170K	169800	1.8	≈0.95	≈0.9	≈0.8	≈1.7
M-IPP 288K	288430	1.8	0.954	0.83	0.86	1.69
D-M[d]	575000	2.4	0.991	0.08	0.22	0.30
Ziegler-Natta fraction						
B-18	651000	3.2	0.981	0.30	–	0.30

(a) Isotactic pentad fraction measured from ^{13}C NMR.
(b) 2,1 additions
(c) Interpolated from intrinistic viscosity/M_W relation
(d) Hoechst exclusive research product

The molecular weight and its distribution were analyzed following standard GPC techniques. The type and concentration of defects were obtained from ^{13}C NMR analysis. Both regio and stereo type defects are found in each of the metallocene poly(propylenes) studied here. Only stereo-type defects are found in sample B-18. The concentration of regio defects was calculated from the intensity of the corresponding NMR peak; that for the stereo-type defects was taken as one half the concentration of *mmmr* pentads. This type of pentad is found twice in any type of stereo defect.

Isothermal crystallizations were carried out in a differential scanning calorimeter, Perkin-Elmer DSC-2B. To avoid any possible memory effects [23], the samples were melted at 207°C for 5–10 min and cooled rapidly to the crystallization temperature. For the relatively low crystallization temperatures, less than 122°C, exotherms were used to obtain the time required for 20% of the transformation to be attained. The crystallization rate was taken as the inverse of this time. At the higher crystallization temperatures the exothermic peak could not be resolved. Here, the extent of the transformation was obtained from the endotherms by measuring the degree of crystallinity with time. Good agreement was obtained between the experimental data measured from both exotherms and endotherms in the crystallization temperature interval between 120 and 123°C.

Results and discussion

The inverse of the time required to attain 20% of the total transformation $1/\tau_{0.2}$ has been taken as a measure of the overall crystallization rate. The natural logarithm of this rate is plotted against the temperature in Fig. 1 for the set of metallocene based poly(propylenes). The weight average molecular weight of these specimens varies from 68480 to 288430 at the same total defect concentration. The open symbols were obtained from analysis of the exotherms while the closed symbols are from the melting endotherms. There is clearly a continuity in the data obtained by the two methods. The major finding illustrated in Fig. 1, is that the data can be represented by a single curve over the range of molecular weights and crystallization temperatures studied. Hence, there is no significant influence of molecular weight on the kinetics. At a given crystallization temperature the crystallization rates are essentially the same for all of the polymers.

These results contrast markedly with the large variation of the rate with molecular weight that is observed for model ethylene-butene copolymers, (hydrogenated poly(butadienes)) [24] and a variety of linear polymers [25–34]. Linear polyethylene is one of the most widely studied systems concerned with molecular weight effects on the crystallization rate. For this polymer a discrete maximum with molecular weight is observed in the rate at most crystallization temperatures [25]. However, at sufficiently low temperature ($\Delta T > 23°$) the

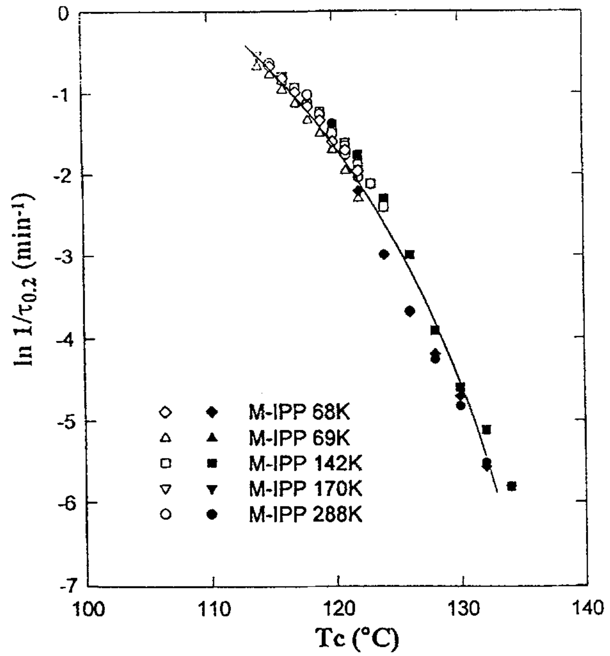

Fig. 1 Plot of natural log of the overall rate of crystallization, $1/\tau_{0.20}$ *vs.* temperature for the poly(propylenes) listed. Open symbols are data from exotherms. Closed symbols from endotherms

maximum is no longer observed and the rate remains essentially constant with chain length. The lack of any molecular weight effect, as is shown in Fig. 1, could be associated to the large undercoolings at which the crystallization is conducted with the poly(propylenes). However, it remains to be determined whether this constancy in crystallization rate with molecular weight that is found here, will still be observed with chains having a smaller concentration of chain defects.

The large negative temperature coefficient of the crystallization rate that is observed in Fig. 1 is a general feature of polymer crystallization. There is a seven-order of magnitude change in the crystallization rate over only a 25 degree range in crystallization temperature. This is clearly indicative of the importance of nucleation in the crystallization process [35]. However, since the crystallization is taking place over a rather large undercooling cognizance must also be taken of the transport term. Utilizing the Turnbull-Fischer expression for the steady state nucleation rate [36], the overall rate of crystallization can be expressed in a general way as

$$1/\tau_{0.20} = k_o \exp\left\{\left(\frac{-E_D}{RT}\right) - \left(\frac{\Delta G^*}{RT}\right)\right\} \tag{1}$$

Here k_o is a constant, ΔG^* is the free energy of forming a nucleus of critical size, and E_D represents the effective activation energy of segmental transport across the crystal-liquid interface. It must be emphasized that Eq. (1) is very general. It applies to all types of nucleation processes and nuclei structures. It does not depend on any specific formulation of the transport term. In order for Eq. (1) to be used in analyzing experimental data certain specific assumptions must be made. The strong negative temperature coefficient, which is typical of nucleation processes, arises from the inherent temperature dependence of ΔG^*.

The form of ΔG^* that is used depends on the specific type of nucleus and nucleation process that is assumed. Several different types of nucleation pro-cesses are usually considered in analyzing polymer crystallization kinetics [35, 37, 38]. These include a three-dimensional nucleus, formed either homogeneo-usly [35] or on certain types of heterogeneities [39], as well as a Gibbs-type two dimensional coherent nucleus [35]. When all the reported experimental kinetic data for polymers are analyzed one has not been able to discriminate between the formation of a three or two-dimensional nucleus [35]. Both models follow either of the theoretical expectations equally well [40]. In all works that have been reported, including the present one, an *ad hoc* assumption needs to be made as to the type of nucleus that is involved. In analyzing the data presented in Fig. 1 we shall assume that a two-dimensional coherent type nucleus is involved. Fortunately the major conclusions that are reached do not depend in any way on the type of nucleus that is selected for analysis. The coherent two-dimensional nucleus is taken for convenience. It does not require or imply that the nucleus be comprised of regularly folded chains. When this type of nucleus structure is adopted, a further assumption is being made that is not required either by nucleation theory or by any known experimental facts.

The expression for ΔG^* for a copolymer with only one type unit participating in the crystal has already been given [24]. Considering the defects as non-crystallizing structural irregularities in the chain, the poly(propylene) molecule can be considered as a copolymer. For a two-dimensional coherent nucleus, ΔG^* of a random copolymer can be expressed as [24],

$$\Delta G^* = 4\sigma_e\sigma_u/(\Delta G_u + RT\ln X_A) \tag{2}$$

Here ΔG_u is the free energy of fusion per repeating unit. It can be approximated in the vicinity of T_m^o by ΔH_u $(T_m^o - T)/T_m^o$. ΔH_u is the heat of fusion per repeating unit and T_m^o the equilibrium melting temperature of the infinite molecular weight homopolymer. σ_u and σ_e are the interfacial lateral and surface free energies per repeating unit and X_A is the mole fraction of crystallizable units. (More generally, for any type of copolymer X_A should be replaced by the parameter p, the sequence propagation probability [41].) The molecular weights that are being studied here are sufficiently high to neglect the influence of finite chain length in the selection of a critical size nucleus [38].

Any expression taken to represent the transport term will be arbitrary since there is no basic theoretical development for this quantity. Okui has been very successful in analyzing a large amount of experimental data by having only to invoke an Arrhenius type activation energy [42]. Quite commonly E_D is taken as the Williams, Landel and Ferry (WLF) activation energy for viscous flow of amorphous polymers [43–45]. In this case E_D is expressed as

$$\frac{C_1C_2T}{T-T_g+C_2}$$

where C_1 and C_2 are WLF-type constants. For polymer crystallization E_D is assumed to characterize the melt activation energy in the vicinity of the growth surface. T_g is the glass transition temperature. Usually this term is given in the form $U^*T/(T-T_\infty)$ with T_∞ as the temperature below which the required segmental motion becomes infinitely slow (T_g-C_2). Two different data sets for the constants U^* and C_2 have been treated as "universal" values. Initially, it was suggested that $U^*=4120$ cal mol^{-1} and $C_2=51.6°$ be used [44]. These values were shown to be inapplicable in a number of cases so that the values $U^*=1500$ cal mol^{-1} and $C_2=30°$C were proposed [46]. It was pointed out later that, in practice the WLF relationship should be used with U^* and C_2 as adjustable parameters [47–51]. Other expressions for the transport term have also been proposed. These include the reinterpretation by Adam and Gibbs [52] of the free volume concept of Doolittle [53] on the basis of configurational free energy changes, as well as and the activation energy for the reptation process [54]. In the present work two sets of U^* and C_2 values were used to analyze the overall crystallization rate data. It has been shown for a variety of polymers that by appropriate selection of U^* and the equilibrium melting temperature the crystallization kinetic data can be linearized in terms of the temperature function given by nucleation theory [47].

With the clear understanding of the basis for the selection of the transport and nucleation terms, Eq. (1) can now be written as

$$\ln(1/\tau_{0.20}) = \ln K_o - \frac{U^*}{R(T-T_\infty)} - \frac{4\sigma_e\sigma_u}{RT(\Delta G_u + RT\ln X_A)} \qquad (3)$$

Accordingly, the basic data given in Fig. 1 have been analyzed according to Eq. (3) and the results are plotted in Fig. 2a and 2b, for the polymers with $M=68480$, 142000 and 288430. In these figures the value of U^* is taken as 1500 cal mol^{-1} and $T_\infty=T_g-30°$. The correct value of T_m^o of the pure isotactic poly(propylene) chain is in dispute. Investigators are divided between those who favor a T_m^o of 186°C [10, 55–59] and those who claim a much higher value

$T_m^o \approx 220°C$ [12, 60–66]. The data shown in Fig. 2(a) are calculated for $T_m^o = 220°C$, while in Fig. 2b T_m was taken as 186°C. Thus, our conclusions will not be based on the, value selected for T_m^o. In both cases the data are well represented by a straight line. The change in T_m^o value only shifts the data along the horizontal axis but does not affect the linear functionality. When the rate data are plotted in this manner a very small molecular weight effect is discerned. However, in other systems there is a greater influence of molecular weight [24–34]. As illustrated in Fig. 3 essentially the same type of results are obtained when U^* and C_2 are taken as 4120 cal mol^{-1} and 51.6° respectively. Curves very similar to those found in Figs 2 and 3 are also obtained when the transport term is completely neglected, i.e. U^* is taken as zero.

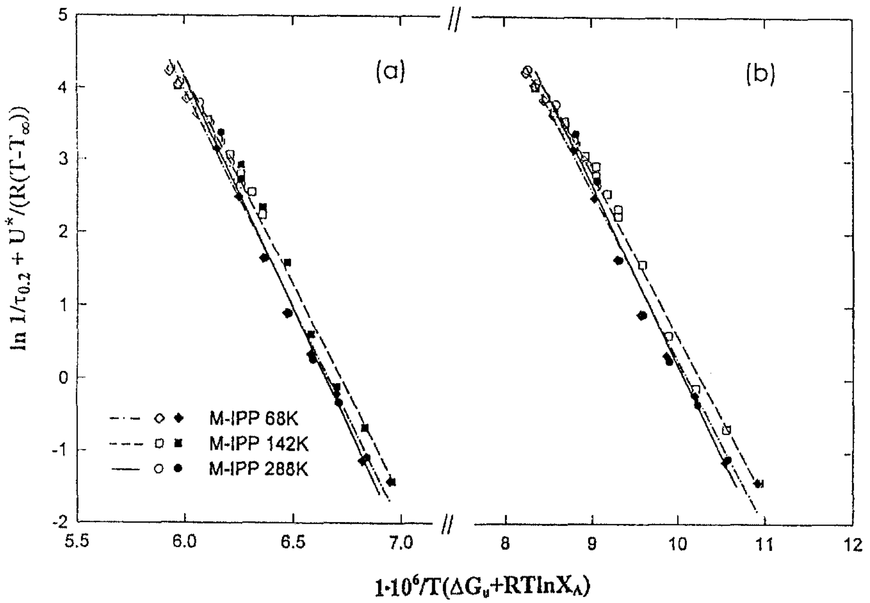

Fig. 2 Plot of overall crystallization rate according to equation 3 for the indicated poly(propylenes). Open and closed symbols as in Fig. 1. ◆ – X_A=0.984, □ - X_A=0.983, ○ - X_A=0.983, U^*=1500 cal mol^{-1}. $T_\infty = T_g - 30°$. $T_g = -15°C$. (a) T_m^o =220°C. (b) T_m^o =186°C

From the slopes of the straight lines, in Figs 2 and 3 the product of the interfacial free energies ($\sigma_e \sigma_u$) can be calculated using Eq. 3. Equation 3 is written assuming that the crystallization process is taking place in Regime I. In this Regime completion of an entire substrate is accomplished before new nuclei are formed. The crystallization rates of the metallocene polymers studied here have been mea-sured in a temperature range for which the spherulite growth rates of unfractionated [1, 8, 12] and fractions of Ziegler-Natta type poly(propylenes) [18] follow Regime II. In this Regime multiple nuclei appear on the substrate because of the rapid increase in nucleation rate [46]. In Regime II:

$$\frac{\Delta G^*}{RT} = \frac{2\sigma_e\sigma_u}{RT(\Delta G_u + RT\ln X_A)} \tag{4}$$

Since no discontinuities are observed in the plots of Figs 2 and 3 we cannot select, or decide, on the specific Regime that is operative for the crystallization of metallocenes. Hence the $\sigma_e\sigma_u$ product is listed in Table 2 considering both Regime possibilities. The specific transport term and equilibrium melting temperature used are also indicated. We have, thus, in this analysis and tabulation, considered a wide range in the values of the parameters involved. We are now in a position to compare the crystallization kinetics of Ziegler-Natta and metallocene poly(propylenes).

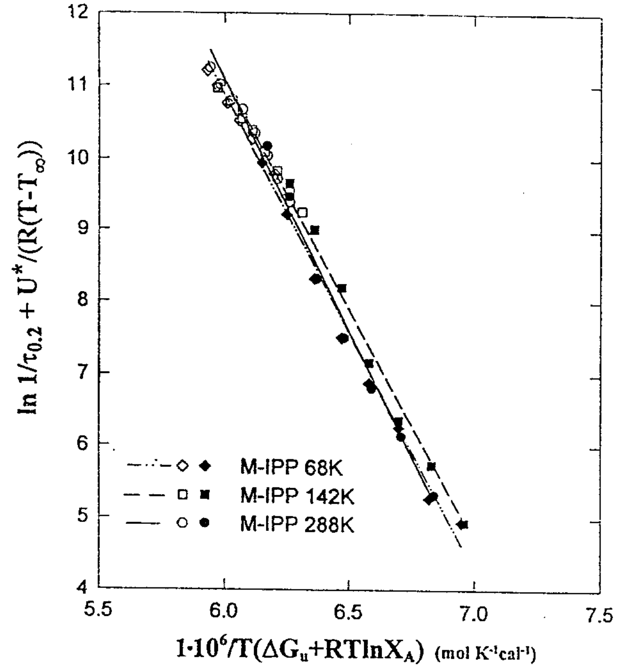

Fig. 3 Plot of overall crystallization rate according to equation 3 for the indicated poly(propylenes). U^*=4120 cal mol^{-1}. $T_\infty = T_g - 51.6°$. $T_g = -15°$C. $T_m^o = 220°$C.
◆ – X_A = 0.984, □ – X_A = 0.983, o – X_A = 0.983

Overall crystallization and spherulite growth rates have been reported and analyzed for unfractionated polymers and fractions of Ziegler-Natta type poly(propylenes). The crystallization rates of the metallocene type poly(propylenes) shown in Fig. 1, and those reported by Marker *et al.* [1] and Godovsky *et al.* [8] obtained by dilatometry can be compared. Although the defect concentration and molecular weights of these poly(propylenes) were not reported it is still instructive to make an initial comparison of the overall crystallization rates.

Table 2 The product of interfacial free energies

Sample	$\sigma_e\sigma_u$ /erg^2 cm^{-4}											
	No transport term				$U^* = 1500$ cal mol^{-1} $C_2 = 30°$				$U^* = 4120$ cal mol^{-1} $C_2 = 51.6°$			
	Regime I		Regime II		Regime I		Regime II		Regime I		Regime II	
	$T_m^o =$ 220°C	$T_m^o =$ 186°C	$T_m^o =$ 220°C	$T_m^o =$ 186°C	$T_m^o =$ 220°C	$T_m^o =$ 186°C	$T_m^o =$ 220°C	$T_m^o =$ 186°C	$T_m^o =$ 220°C	$T_m^o =$ 186°C	$T_m^o =$ 220°C	$T_m^o =$ 186°C
M-IPP 68K	1125	433	2250	866	1227	472	2454	944	1348	519	2696	1038
M-IPP 142K	1088	419	2176	838	1190	458	2380	916	1328	503	2656	1006
M-IPP 288K	1244	466	2488	932	1299	507	2598	1014	1424	556	2848	1112

In the region of low crystallization temperatures (115–120°C), the metallocenes of this work and the unfractionated poly(propylenes) studied by Marker *et al.* [1] and Godovsky *et al.* [8] have very similar rates. However, the metallocenes give much slower kinetics in the highest T_c range (≈135–140°C). Cheng *et al.* were able to measure spherulite growth rates of fractions over a much wider temperature interval than studied here. Their growth rate *vs.* temperature curve exhibits a break at ≈135°C. Although not as marked, a break at this temperature was also reported by Monasse and Haudin [12]. Because of the time involved, the crystallization of the metallocenes was not studied beyond 135°C. It is an open question at this point if the break will also be found for this type of poly(propylenes). Smooth curves were found in the variation of the crystallization rate with temperature for all the molecular weight samples studied here.

The slopes of the straight lines in Figs 2a and 2b are approximately double the value found by Monasse *et al.* [12], by Marker *et al.* [1] and Godovsky *et al.* [8]* for unfractionated Ziegler-Natta polymers. They are also significantly higher than the value obtained by Cheng *et al.* [18] for a fraction, PP(Y-9), of about the same isotacticity level. Considering T_m^o for this fraction of 180.2°C, these latter authors obtained a $\sigma_e\sigma_u$ value of 827 erg^2 cm^{-4} from the growth rate data that was adjusted to Regime II. The product $\sigma_e\sigma_u$ of metallocene M-IPP 288 K analyzed with similar values of T_m^o (186°C) and transport term, is higher (1014 erg^2 cm^{-4}). Thus, there is evidence from both growth and overall crystallization kinetics data to conclude that metallocene type poly(propylenes) show much higher values of $\sigma_e\sigma_u$ than either unfractionated or fractions of Ziegler type poly(propylenes). If we make the reasonable assumption that σ_u is the same for both type of poly(propylenes), then the ilmportant conclusion can be made that the metallocene type poly(propylenes) show considerably higher surface interfacial free energies.

If we consider that all or most of the defects are excluded from the crystalline lattice and preferentially accumulated on the surface of the crystal, the surface of the Ziegler-Natta poly(propylenes) will contain only stereo type defects while that of the metallocenes will have both stereo and regio (2,1 addition) type defects. Thus, the higher interfacial free energies of the metallocenes are interpreted as being a consequence of the presence of the regio type defects in the interfacial region. This leads to the conclusion that the regio defects lead to the development of a more disordered and strained interface on the 001 surface of the poly(propylene) crystal.

It is clear that when properly analyzed the comparison should be made in terms of the chain defect concentration rather than isotacticity content. How-

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* To make this comparison the $\tau_{0.20}$ data were extracted from the dilatometric data reported in these works [1, 8] and plots similar to that of Figs 2a and 2b constructed.

ever, the details of the NMR characterization were not given in the reported literature works. Hence, to verify the above conclusion, the overall crystallization rates of a well characterized Ziegler fraction (B-18) and a metallocene type poly(propylene) were studied. A detailed ^{13}C NMR analysis and GPC characterization are available for both samples. As stated above, these samples were chosen for being a matched pair in terms of molecular weight and the total defect concentration. The key molecular factors of these two polymers are also listed in Table 1. The molecular weights are appreciably higher than the other metallocene poly(propylenes) studied here and the defect concentration is reduced by a factor of about five. The Ziegler-Natta fraction only contains stereo defects, while regio type defects predominate in the metallocene type polymers.

The overall crystallization rate of these two polymers is shown in Fig. 4 as a function of crystallization temperature. A smooth, continuous decrease of the rates is observed with increasing temperature. At the low and medium crystallization temperatures the metallocene type polymer shows a considerably higher crystallization rate than its Ziegler counterpart. However, it is interesting that at the highest crystallization temperatures, the rates of both poly(propylenes) coincide and probably cross over one another.

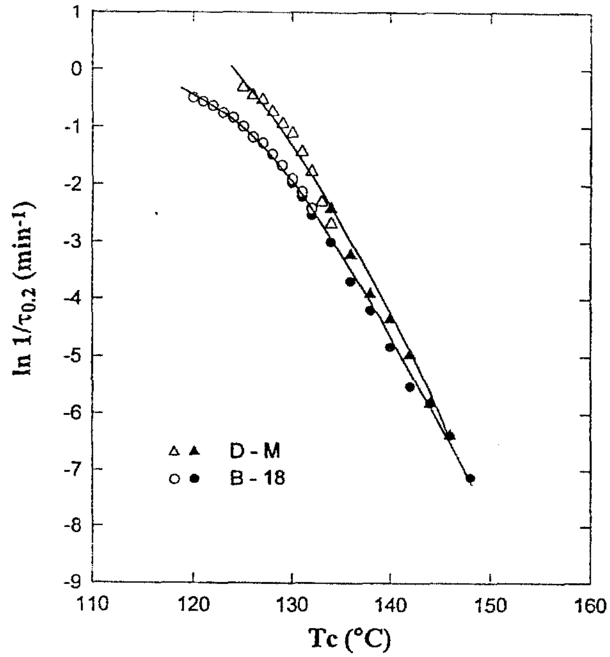

Fig. 4 Plot of natural log of the overall rate of crystallization, $1/\tau_{0.20}$, of a Ziegler poly(propylene) fraction and a metallocene poly(propylene), of matched molecular weight and defect composition, *vs.* crystallization temperature. Open and closed symbols same as in Fig. 1

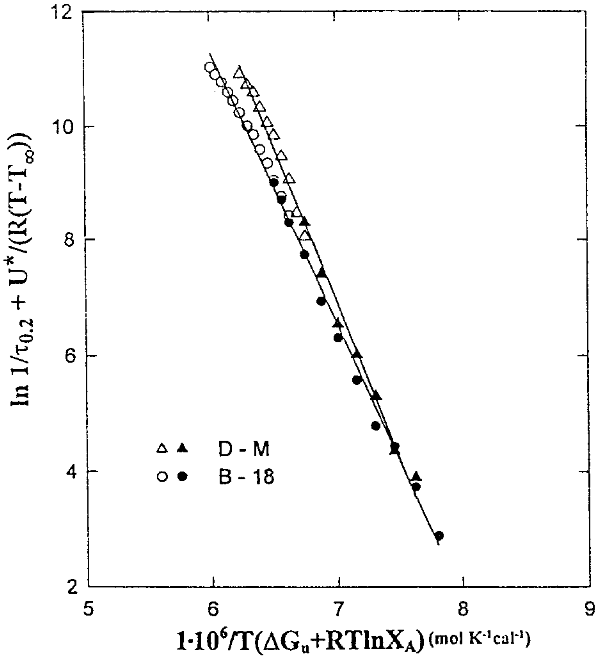

Fig. 5 Plot of overall crystallization rate according to Eq. (3) for data taken from Fig. 4. T_m^o =220°C. U^*=4120 cal mol^{-1}. T_∞ =T_g−51.6°. T_g =−15°C. X_A =0.997

The differences in the variation of the crystallization rates with temperature between these two types of poly(propylenes) became better defined when the rates are analyzed according to classical nucleation theory according to Eq. 3. The results are shown in Fig. 5. Except for the data obtained at the very lowest temperature, both sets of data can be fitted to straight lines over the whole interval of temperatures studied. The data in this figure extend to crystallization temperatures as high as 145°C. There is not any evidence at this point of a characteristic Regime transition. The same functionality (except for numerical values) is observed with no transport term at all or if the values U^* =1500 cal mol^{-1} and C_2 =30° are used. The use of either T_m^o = 220°C or T_m^o =186°C does not change the linearity of the analysis shown in Fig. 5. It is clear that both poly(propylenes) have very different slopes and, hence, different values of the product $\sigma_e\sigma_u$. The metallocene type poly(propylene) (D-M) having mostly regio type defects shows significantly higher $\sigma_e\sigma_u$ than the Ziegler fraction with only stereo defects. The $\sigma_e\sigma_u$ values are listed in Table 3. The possibility that the data may conform to Regime I or to Regime II is considered and the calculated data using two sets of constants are listed in this table. The $\sigma_e\sigma_u$ values corroborate the above conclusion made with the series of metallocenes having different molecular weights and reveal important aspects specific to the phase

Table 3 The product of interfacial free energies $\sigma_e\sigma_u$

Sample	$\sigma_e\sigma_u$/erg^2 cm^{-4}											
	No transport term				$U^* = 1500$ cal mol^{-1} $C_2 = 30$°C				$U^* = 4120$ cal mol^{-1} $C_2 = 51.6$°C			
	Regime I		Regime II		Regime I		Regime II		Regime I		Regime II	
	$T^o_m =$ 220°C	$T^o_m =$ 186°C	$T^o_m =$ 220°C	$T^o_m =$ 186°C	$T^o_m =$ 220°C	$T^o_m =$ 186°C	$T^o_m =$ 220°C	$T^o_m =$ 186°C	$T^o_m =$ 220°C	$T^o_m =$ 186°C	$T^o_m =$ 220°C	$T^o_m =$ 186°C
B-18	812	288	1624	576	894	319	1788	638	999	353	1998	706
D-M	968	331	1935	662	1044	359	2088	719	1149	392	2298	784

structure of the two types of polypropylene crystals. The differences in slopes can be interpreted as being a consequence of having different surface free energies or it could also be a consequence of having different sequence propagation probabilities, *i.e.*, different value of X_A. In this latter case, the metallocene poly(propylenes) would present a higher value of X_A than the Ziegler poly(propylene).

The interpretation that the metallocene type poly(propylene) has higher interfacial free energy than the matched Ziegler fraction is in agreement with the preferential rejection of the defects to the surface of the crystallite. It is also of interest to notice that the product $\sigma_e\sigma_u$ does not change appreciably with molecular weight (Table 2). However, it does change with defect content. The D-M metallocene with a lower defect content gives smaller slopes (or product $\sigma_e\sigma_u$) than those reported in Table 2. It is logical that if the defects are preferentially accumulated in the surface a decreased number of defects will lead to a lower value of σ_e.

In analyzing the data in Fig. 5 one should also consider the possibility that the two types of polymers have different spreading rates, *g*. This is an important parameter characterizing Regime II [67]. Consequently, different slopes could be expected from this source.

Conclusions

No influence of molecular weight on the crystallization kinetics was found in the analysis of a series of metallocene type poly(propylenes) with constant isotacticity content ≈ 0.95 and about 1.7 mol% of defects. The temperature coefficient of the crystallization process was also found to be essentially independent of molecular weight in the M_W range studied (68480 to 288430). The application of classical nucleation theory to the data resulted in continuous straight lines of basically the same slope indicative of formation of crystals with very similar values for the product $\sigma_e\sigma_u$.

Most significant is the fact that the metallocenes show significantly higher $\sigma_e\sigma_u$ value than a Ziegler-type poly(propylene) fraction having a matched molecular weight and defect concentration. This result was found from a comparison with literature data as well as a direct independent study of a metallocene/Ziegler matched pair. The difference is interpreted as a consequence of the defects being excluded from the lattice during the crystallization process and preferentially located on the surface of the crystallite. The metallocenes with both regio and stereo defects in the chain appear to have higher interfacial free energies (σ_e) than their Ziegler counterpart with only stereo defects. However, a different sequence propagation probability between the two types of chains, or differences in spreading rates, could also explain the observed difference.

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