Crystallization kinetics of isotactic poly(1-hexadecene)

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The crystallization kinetics of the isotactic content of three poly(1-hexadecene) (PHD) samples with different tacticity has been analysed by differential scanning calorimetry (d.s.c.), using both isothermal and non-isothermal treatments. Two d.s.c. peaks are found in both the melting and cooling of the three PHDs. The high- and low-temperature peaks are attributed to the crystallites formed by the isotactic and atactic chains, respectively. Additional small-angle X-ray diffraction (SAXD) experiments, using synchrotron radiation, have been performed, indicating that the isotactic crystals exhibit appreciably smaller spacings than the atactic ones. Because of overlapping problems, only the isothermal crystallization kinetics of the isotactic content can be studied. The corresponding analysis in the range of crystallization temperatures from 36 to 45°C showed that the process can be described by the Avrami equation up to relatively high conversions. The rate constant k of this equation increases very rapidly with undercooling (about four orders of magnitude in only 8 degrees), indicating that the process is controlled by the nucleation. The value of the Avrami exponent is approximately 4, suggesting a homogeneous nucleation followed by three-dimensional growth. The melting temperature of the isotactic content is independent of the crystallization temperature and was found to be 58°C. The study of the non-isothermal crystallization of PHDs shows that it can be analysed in terms of an Avrami-type equation and similar mechanisms of nucleation and growth apply to all temperatures and cooling rates in the ranges studied. Moreover, the Avrami exponent in this analysis is of the same order as in the case of isothermal treatment.

(Keywords: isotactic poly(1-hexadecene); comb-like polymers; crystallization kinetics)

INTRODUCTION

Comb-like polymers are a special kind of macromolecules with properties well differentiated from those of linear and branched polymers[1]. These special properties are the result of the existence of relatively long branches regularly spaced every few atoms of the main chain. If these lateral branches are sufficiently long, a very high intramolecular ordering is developed. Thus, crystalline structures similar to those of low-molecular-weight lipids are formed in the case of lateral paraffinic segments exceeding about 8–10 methylene groups[2,3]. Moreover, the presence of mesogenic groups in the lateral branches will result in the known side-chain liquid-crystalline polymers.

Focusing on the polymers with long paraffinic branches, it is believed that the outer segments beyond 8–10 methylenes will be included in a crystal lattice, while the segment closer to the skeleton, and the main chain itself, will remain in an amorphous layer. Thus, their temperatures and enthalpies of fusion are essentially independent of the nature of the main chain and they change as a function of the length of the lateral branch[2,4,5]. Considering this picture, the outer crystallizable part of the branch is envisaged with a very high degree of motion in the amorphous state, as in liquid paraffins, but its connection to the main chain, with restricted mobility, cannot be disregarded. The study of the crystallization kinetics of these comb-like polymers is therefore of great interest.

It is well known that the crystallization of chain-folded polymers is described by nucleation and growth processes and the rate of transformation can be analysed by the Avrami equation[6]. The mesophase formation in liquid crystals, both polymeric[7–12] and low-molecular-weight compounds[13–15], can also be described by this equation. On the other hand, studies on the crystallization kinetics of comb-like polymers are scarce.

Another important aspect of comb-like polymers which affects their crystallization ability is the stereochemistry of the main chain. For instance, our studies on high terms of poly(α-olefin)s showed that only the isotactic content of poly(1-decene) is able to crystallize[16]. In contrast, both the isotactic and atactic content of poly(1-hexadecene) (PHD) seem able to crystallize, and the two peaks found in the differential scanning calorimetry (d.s.c.) melting pattern of samples of PHD with different tacticity have been assigned to the melting of atactic and isotactic chains[17].

The purpose of this work is to analyse, using d.s.c., the crystallization kinetics of three samples of PHD

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with different tacticity. Both isothermal and non-isothermal treatments, based on Avrami-type equations, are employed, in order to test the applicability of these equations. Moreover, a further insight into the structure of these polymers is obtained from additional diffraction data.

EXPERIMENTAL

Three samples of PHD with different isotactic content have been studied. The details of their synthesis and characterization were previously reported[17]. Briefly, a $MgCl_2$-supported $TiCl_4$ catalyst was used for the polymerization of 1-hexadecene and the different tacticities were provided by the addition of Lewis bases to the catalyst[17]. The isotactic contents and molecular weights of the three samples are shown in *Table 1*.

The calorimetric analysis was carried out in a Perkin–Elmer DSC7 calorimeter, connected to a cooling system and calibrated with different standards. Both isothermal and non-isothermal methods were used for the analysis of the crystallization kinetics of the three PHD samples. In the latter case, the samples were cooled from the melt (75°C) at different rates, in the range 1–15°C min^{-1}, and then melted at 10°C min^{-1}. For the isothermal experiments, the samples were brought from the melt to the desired crystallization temperature, T_c, and the heat evolution was registered as a function of time. The values of T_c ranged from 36 to 45°C. The melting temperatures of these isothermally crystallized samples were determined by heating from the corresponding T_c at 5°C min^{-1} after crystallization was complete. This lower rate was chosen because of the relatively small undercoolings involved. In all cases, peak temperatures were considered.

Small-angle X-ray diffraction (SAXD) profiles were obtained at Daresbury Laboratory (station 8.2) using synchrotron radiation. A quadrant detector was employed at a distance of 3.2 m from the sample. The spacings covered by the experimental set-up ranged from about 60 to 2.7 nm. Rat-tail collagen ($l = 67.0$ nm) was used for calibration.

RESULTS AND DISCUSSION

Thermal transitions and diffraction experiments

The d.s.c. melting curves of PHDs show two endothermic peaks which have been assigned[17] to the crystallites of isotactic and atactic polymer. Moreover, two exothermic peaks are also obtained when the samples are cooled from the melt. The corresponding cooling and heating cycles for the PHD2 sample are presented in *Figure 1*. The temperatures of these transitions are not very dependent on the stereoregularity of the sample, as can be seen in *Table 2*. This is especially true for the higher-temperature peak, attributed to the isotactic chains. Larger differences are found for the transitions belonging to the atactic crystallites. This is not very significant, considering the broadness of the corresponding peaks and the very high sensitivity of the atactic crystallites to subtle changes in the thermal history. Concerning this point, the melting temperature of this low-temperature peak is very much affected by annealing. For example, the lower curve of *Figure 2* represents the melting of a PHD1 sample which was left for several days at room temperature (which could be higher than 30°C during the day), then loaded into the

Table 1 Isotactic content and molecular weight of the three poly(1-hexadecene) samples[17]

	Isotactic content		
Sample	d.s.c.	n.m.r.	$10^{-4} M_v$
PHD1	0.39	0.43	7.8
PHD2	0.66	0.62	2.8
PHD3	0.92	0.91	1.8

Table 2 Peak temperatures for the transitions and total enthalpies of melting of the three poly(1-hexadecene) samples cooled and heated at 10°C min^{-1}

Sample	T_{c1} (°C)	T_{c2} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m^{total} ($J g^{-1}$)
PHD1	18	29	28	60	94
PHD2	16	32	26	60	98
PHD3	24	33	23	59	107

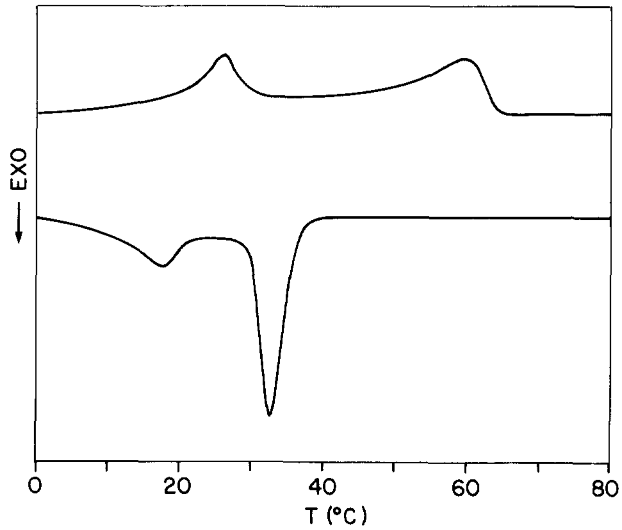

Figure 1 D.s.c. curves of a PHD2 sample cooled from the melt (lower curve) and the subsequent heating (upper curve). Cooling and heating rates: 10°C min^{-1}

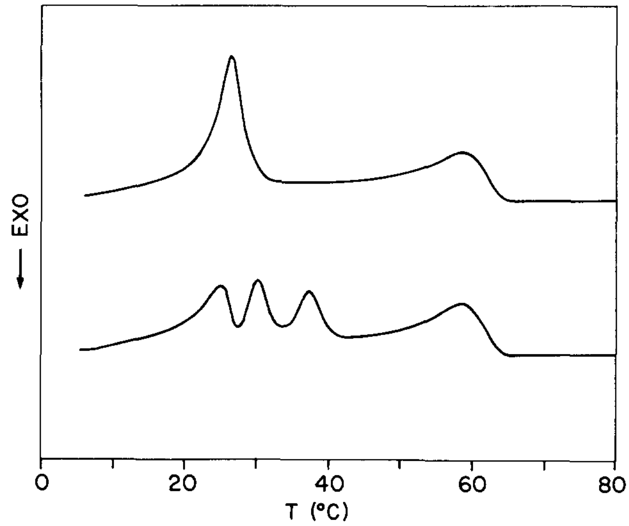

Figure 2 D.s.c. melting curves of a PHD1 sample. Lower curve: sample crystallized for a long time at room temperature, loaded into the calorimeter at 25°C and registered from 0°C. Upper curve: sample crystallized by cooling from the melt. Scanning rates: 10°C min^{-1}

calorimeter at 25°C and its melting registered from 0°C. Three peaks, corresponding to the three different annealing conditions involved, are observed in the low-temperature region. This melting pattern is very different from that of the sample crystallized by cooling from the melt at 10°C min^{-1} (upper curve in *Figure 2*), although the total enthalpy is exactly the same. The conclusion is that the degree of perfection of the crystallites formed by the atactic polymer is very much dependent on the annealing temperature and it seems that at least a part of the atactic chains may organize, after appropriate annealing, into a structure very close to that of the isotactic crystals.

On the other hand, the high-temperature peak is rather insensitive to the thermal history. Thus, the melting temperatures reported for T_{m2} in *Table 2* are the same as those obtained when the PHD samples are isothermally crystallized at temperatures in the range 36–45°C (see below). Moreover, the annealing of the samples at high temperatures where some of the isotactic chains are also molten (55°C, for instance) produces a slight change of the shape of the melting peak due to that partial melting, but the temperature of the disappearance of the last trace of crystallinity remains constant.

One implication of this crystallization behaviour is that only the crystallization kinetics of the high-temperature peak can be studied. Thus, if the temperature is high enough, only the isotactic content will be able to crystallize. However, if the temperature is lowered to the region where the crystallization of the atactic chains can proceed at the time-scale of the calorimeter, it will appear overlapped to the end of the formation of the isotactic crystals. At present, we are trying to obtain a completely atactic sample of PHD to be able to analyse its crystallization kinetics and to investigate the implications for the structure of different annealing conditions, which may lead to multiple melting peaks like those ones in the lower curve of *Figure 2*.

Considering now the total enthalpies of melting of PHDs (see right hand column of *Table 2*), it has been deduced[17] that the enthalpy takes the value of 110 J g^{-1} for the pure isotactic polymer and is of the order of 85 J g^{-1} for the atactic one. These figures are considerably smaller than those of n-paraffins[18], where the calculated values are of the order of 260–280 J g^{-1} and the experimental ones about 210–230 J g^{-1}. This is not surprising, taking into account that the crystallinity deduced[17] from the WAXD diagrams in the PHD samples is of the order of $40 \pm 15\%$. Considering this crystallinity, the enthalpy of fusion of a perfectly crystalline PHD sample may be very close to that for the n-paraffins or the theoretical value for 100% crystalline polyethylene[19]. Moreover, a value of about 40% crystallinity for PHD is in good agreement with that expected if only those carbons exceeding the limit of 8–10 carbons being part of the crystal.

In principle the lateral crystallization of comb-shaped polymers can be considered as an extended-chain crystallization, as seen in n-paraffins or very-low-molecular-weight polyethylene. However, considering the restricted crystallinity of PHD, the crystallization process of this polymer will differ from both chain-folded and extended-chain crystallization.

The next issue is the structural difference between isotactic and atactic crystals of PHD. As has been pointed out[2], the enthalpies of fusion of long-chain polyolefins do not depend very much on stereoregularity, although the melting points of the isotactic crystals are considerably higher than those of the corresponding atactic ones, as confirmed in this work. This difference has been ascribed[2] to distinct steric configurations of the main chain and crystalline structure. Thus, in the isotactic crystals the main chain assumes a helical conformation[2,20] which obliges the side branch to bend apart while the atactic crystals of polyolefins present a structure similar to other comb-like polymers with the side groups perpendicular to the main chain axes.

As we did not find significant differences in the WAXD patterns of the three PHD samples[17], the polymers were analysed by SAXD, using synchrotron radiation. As expected, no long spacing was detected at the usual values of chain-folded polymers (up to the experimental limit of 60 nm). However, clear maxima were found at values of the scattering vector, *s*, near 0.3 nm^{-1}, as it can be observed in *Figure 3*. These SAXD profiles are clearly dependent on the tacticity of the polymer, in such a way that the maxima correspond to 3.42 ± 0.07, 3.29 ± 0.05 and 3.21 ± 0.04 nm for samples PHD1, PHD2 and PHD3, respectively. (This spacing corresponds to the Type II crystal form reported by Turner Jones[20]. Only this crystal form has been detected in the samples analysed here, i.e. those isothermally crystallized or cooled from the melt at controlled rates.)

In contrast to the d.s.c. results, no bimodal behaviour is observed in these SAXD patterns, although a deconvolution of the peaks can be performed as the profiles are clearly dependent on the tacticity. Taking into account the stereoregularity of the samples (see *Table 1*), the corresponding results indicate the following spacings of the maxima: 3.6 ± 0.1 nm for a pure atactic sample and 3.21 ± 0.04 nm for a pure isotactic PHD polymer.

The smaller value of the spacing for the isotactic crystals agrees with the structural model mentioned before, of the side chain being tilted with respect to the main chain in the isotactic polymer. The spacing

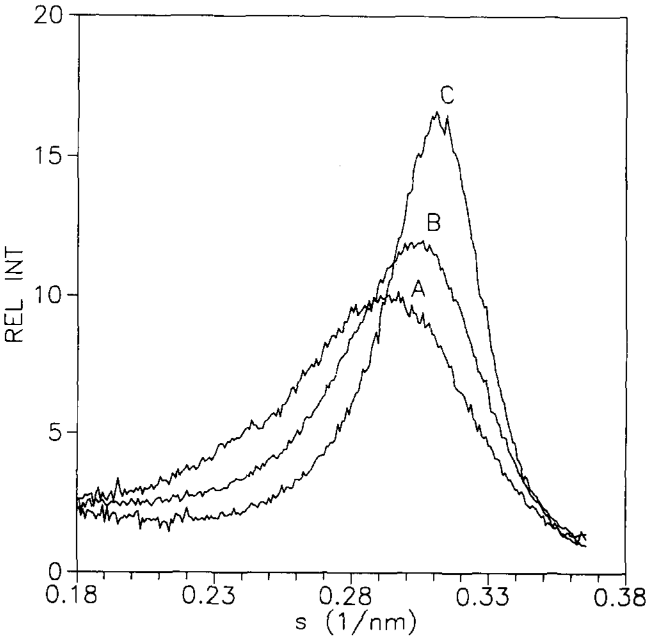

Figure 3 SAXD profiles for the three PHD samples, acquired at room temperature (21°C): (A) PHD1, (B) PHD2 and (C) PHD3

calculated[20] between two parallel main chains with fully extended zig-zag side chains is 4.03 nm. Therefore, a tilting angle of about 37° might be involved in the isotactic crystals. The estimated value for the atactic crystal is also considerably smaller than 4.03 nm. However, if the first 8–10 carbons are amorphous, they may be disposed in a less expanded conformation involving *gauche* states and the estimation of tilting angle may not be straightforward. (Unfortunately, we were not able to stretch the samples, and extract information about a possible tilting angle from the diffractograms of oriented samples.)

Isothermal crystallization of isotactic poly(1-hexadecene)

The three poly(1-hexadecene) samples were isothermally crystallized in the temperature range 36–45°C. At higher temperatures, the crystallization rate is too slow and the integration errors become very big. On the other hand, the time-scale of the experiments at temperatures lower than 36°C is so small that the process begins before the time necessary for temperature equilibration in the calorimeter. Moreover, the crystallization of the atactic chains is appreciable at those lower temperatures, overlapping the isotactic exotherm.

Typical isothermal curves are presented in *Figure 4*. From these curves, the extent of the crystallization at time t, $X_c(t)$, is determined as the ratio of the enthalpy evolved at time t to that of the overall process.

From these data, the crystallization kinetics has been analysed in terms of the Avrami equation[21–23]:

$$X_c(t) = 1 - \exp(-kt^n) \qquad (1)$$

where k is a kinetic constant of the crystallization process and the exponent n is a parameter defining the mode of nucleation and crystal growth geometry[6]. The representations of this equation in the usual double logarithmic plots for the three PHD samples are shown in *Figures 5, 6* and *7*. It can be observed that the Avrami equation is followed up to relatively high conversions. The values of k and n were obtained by linear least-squares fits of the data in the initial linear portions of each isotherm. These values are collected in *Table 3*. It can be observed that, within experimental error, the Avrami exponent n is independent of the crystallization

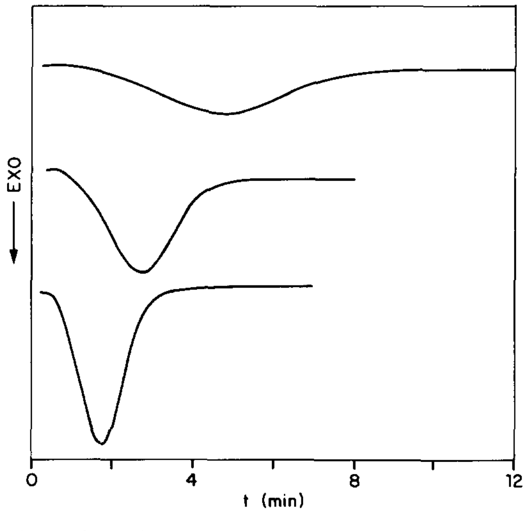

Figure 4 Isothermal crystallization thermograms of the isotactic content of a PHD1 sample at three different temperatures, 42, 40 and 38°C, from top to bottom, respectively

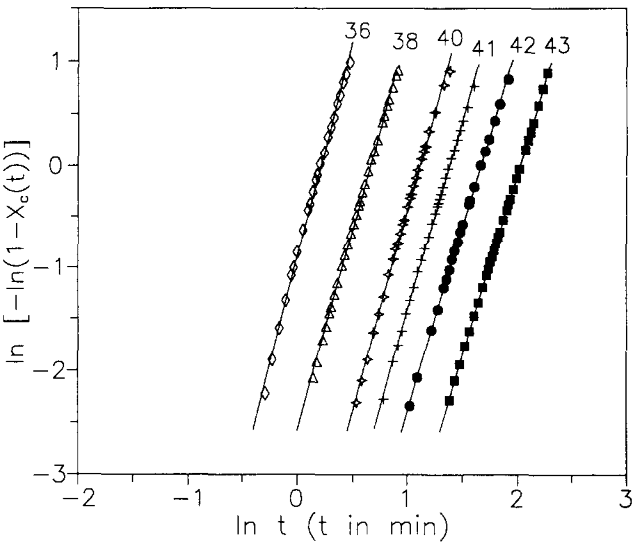

Figure 5 Avrami plots of sample PHD1 crystallized at the indicated temperatures

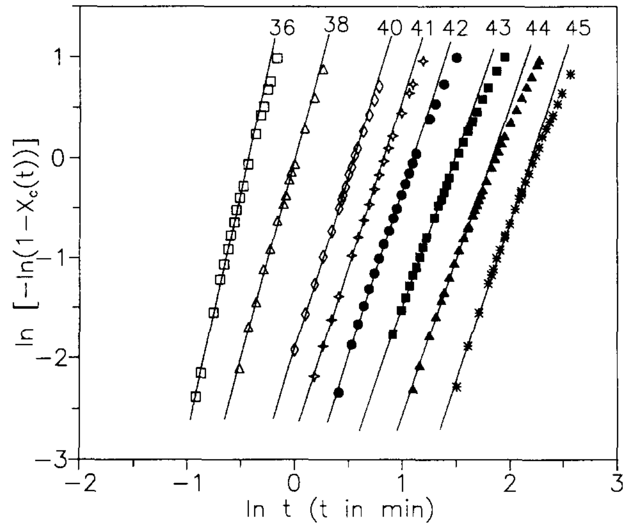

Figure 6 Avrami plots of sample PHD2 crystallized at the indicated temperatures

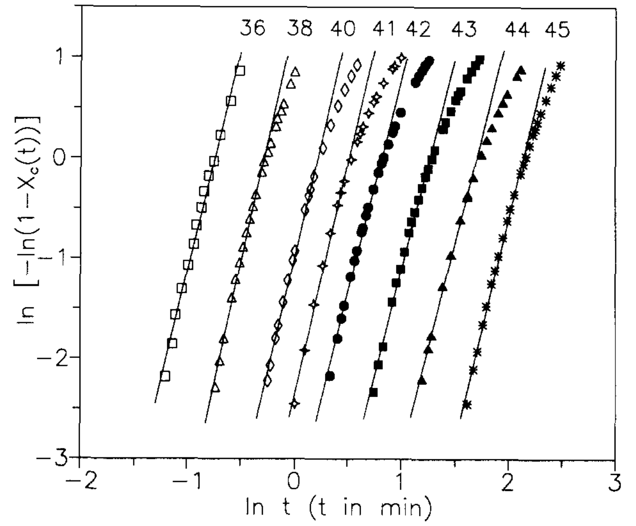

Figure 7 Avrami plots of sample PHD3 crystallized at the indicated temperatures

Table 3 Avrami parameters for the isothermal crystallization of the isotactic content of the three poly(1-hexadecene) samples

T_c (°C)	ΔT (°C)[a]	Avrami exponent, n			k (min^{-n})		
		PHD1	PHD2	PHD3	PHD1	PHD2	PHD3
45	13		3.2	3.8		8.86×10^{-4}	2.46×10^{-4}
44	14		3.1	3.3		3.45×10^{-3}	2.96×10^{-3}
43	15	3.6	3.1	3.3	7.30×10^{-4}	9.95×10^{-3}	1.22×10^{-2}
42	16	3.6	3.3	3.3	2.45×10^{-3}	2.65×10^{-2}	5.46×10^{-2}
41	17	3.7	3.3	3.4	5.70×10^{-3}	6.49×10^{-2}	1.36×10^{-1}
40	18	3.9	3.4	3.8	1.32×10^{-2}	1.49×10^{-1}	3.57×10^{-1}
38	20	3.9	3.9	4.2	7.64×10^{-2}	9.60×10^{-1}	2.89×10^{0}
36	22	4.2	4.8	4.3	4.10×10^{-1}	8.05×10^{0}	2.51×10^{1}
		$\bar{n}$ 3.8±0.3	3.5±0.6	3.7±0.4			

[a] Actual undercooling $\Delta T = T_m - T_c$

temperature, and a value close to 4 is found for the three samples, although the results for PHD2 are rather scattered. A dependence of n on the molecular weight and/or the tacticity of the sample cannot be disregarded. However, considering the intermediate tacticity and molecular weight of the PHD2 sample (see *Table 1*), we think that the differences in *Table 3* may be explained just by experimental error. The interpretation of the values of n is, then, that the primary nucleation of these PHD samples seems to be homogeneous followed by a three-dimensional growth.

The values of the overall rate constant, k, increase with the undercooling in a similar way for the three samples: approximately four orders of magnitude for an interval of 8°C, in the range of T_c studied here, i.e. the dependence of the overall rate of crystallization on T_c is very large, exhibiting a negative temperature coefficient. All these facts support a nucleation-controlled overall crystallization process. Unfortunately, any attempt to study the nucleation (and growth) process by optical microscopy was unsuccessful, as homeotropic textures seem to be involved in these PHD samples.

Considering the absolute values of k, it can be observed in *Table 3* that, for most of the temperatures, the rate constant follows the order PHD1 $\leqslant$ PHD2 < PHD3. One of the reasons for this change may be the variation in the molecular weights (see *Table 1*). Moreover, as we are considering the crystallization of the isotactic chains, it is also likely that the increase of the atactic content may have some effect on the overall rate of crystallization.

A better picture of the effect of temperature on the crystallization rate can be obtained from *Figure 8*, where the crystallization rate has been expressed as the inverse of the time, $\tau_{0,1}$, necessary to obtain a 10% transformation, and plotted against T_c (similar behaviour is obtained if the time to reach 50% transformation is considered). It can be observed that PHD2 and PHD3 exhibit similar crystallization rates, while PHD1 crystallizes more slowly at a given T_c. Moreover, very fast rates are obtained at low actual undercoolings, $T_m - T_c$, and the sensitivity to temperature is very high. This is not surprising, taking into account the special characteristics of side-chain crystallization, with a presumably low activation energy barrier. We have found a very similar behaviour in mesophase formation from the isotropic melt in liquid-crystalline polyesters[24].

The melting temperature of these isothermally crystallized samples has been also analysed. The plot of T_m *versus* T_c for the crystallization of the isotactic content of the three PHD samples is presented in *Figure 9* (the difference between these values and those in *Table 2* is due to the variation in the heating rate: 5 and 10°C min^{-1}, respectively). It can be observed that, within experimental error, T_m is not dependent on T_c, i.e. the degree of perfection of the crystals seems to be unchanged. Moreover, about the same value is obtained for the three samples, averaging 57.6°C. (A value of approximately 62°C is obtained if the melting temperature is taken as that of the disappearance of the last trace of crystallinity instead of peak temperatures.) These melting temperatures are close to those for the n-paraffin of 28 carbons in length[18], which seems to contradict the expectations of only the outer carbons in the lateral branch participating in the crystal. However, the effect of the main chain on the organization of the crystallites cannot be disregarded. Solid-state n.m.r. experiments are in progress in order to extract more information about the structure of these side-chain polymers.

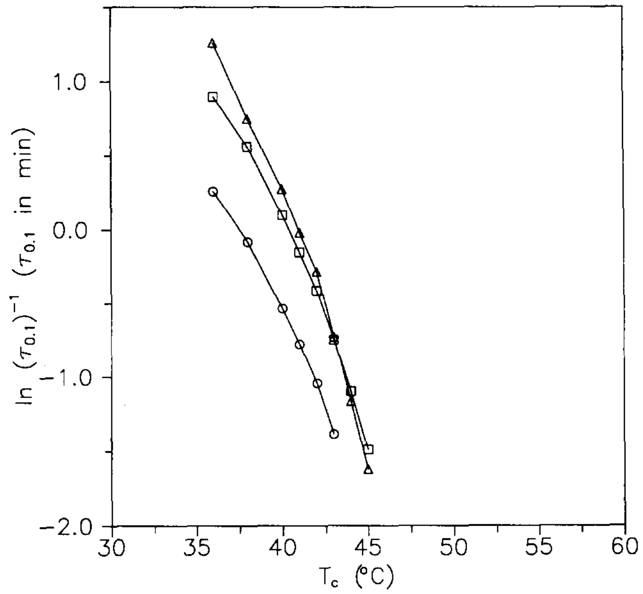

Figure 8 Plot of ln $(\tau_{0.1})^{-1}$ as a function of T_c for the three PHD samples: (○) PHD1; (□) PHD2; (△) PHD3

Although a variation of T_m with T_c might be regarded for lower undercoolings than those considered here, this supposition is unlikely when considering the annealing experiment at 55°C (see above). Therefore, it is expected that the thickness of the crystallites will be constant and the three-dimensional order will be developed by growing in the two directions perpendicular (ideally) to the lateral chain. Thus, these crystals will resemble those of the n-paraffins except for the reduced crystallinity imposed by the presence of the main chain.

Of course, as the length of the lateral branch (or the number of carbons in the n-paraffin) increases, the melting temperature increases[1,2,18], the limit being the polyethylene chain. The qualitative difference is that in our case the crystals are always extended, in contrast to polyethylene where the most usual case is to have chain-folded crystals with actual T_m different from T_m^0, the melting temperature of a perfectly extended crystal. However, it has been shown[25] that even high-molecular-weight n-alkanes do exhibit a variation of T_m with T_c, despite the formation of extended-chain crystals. The reason given[25] is that molecular crystals are not formed and the complete molecule does not participate in the initial nucleus.

The lateral crystallization of chain molecules is, therefore, a complex case, and although the crystallization of side-chain polymers implies several aspects in common with n-paraffins, the effect of the main chain on a possible reduction of the melting temperature and crystallinity may have also an important role. These considerations have to be taken into account when applying any of the current theories developed for extended-chain crystallization[25,26].

Non-isothermal crystallization

The study of the non-isothermal crystallization kinetics can be a very good alternative to the isothermal one specially in those cases where the transformation is very fast, as in our case or in the mesophase formation, where the temperature range for measurable isothermal rates is very limited.

The majority of the formulations proposed for non-isothermal studies are based on Avrami-type equations. One of the more usual theories is that of Ozawa[27], where it is assumed that when a polymer is cooled from the melt at a certain rate the crystallization at a given temperature proceeds from a distribution of nuclei growing at a constant rate. With this assumption, the Ozawa equation reads[27]:

$$-\ln(1-X_c)=\frac{k(T)}{v^n} \qquad (2)$$

where X_c is the degree of transformation at a temperature T, v is the cooling rate, n is again the Avrami exponent and $k(T)$ is a cooling crystallization function, which depends exponentially on T and includes the free energy term of the process[27]. (The Ozawa equation can also be used in the non-isothermal crystallization from the quenched state and then v is the heating rate and $k(T)$ a heating function.)

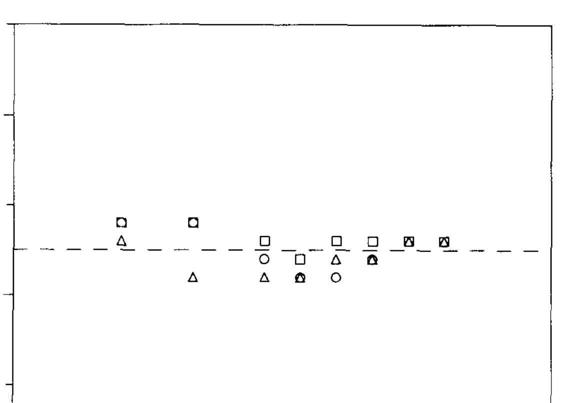

Figure 9 Melting temperatures as a function of the crystallization temperatures for the three poly(1-hexadecene) samples: (○) PHD1; (□) PHD2; (△) PHD3

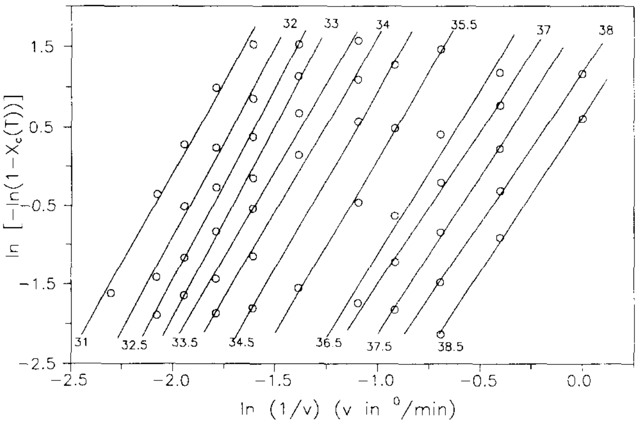

Figure 10 Representation of the Ozawa equation for sample PHD1

This treatment has been applied to our PHD samples in the range of cooling rates from 1 to 15°C min^{-1} (chosen for practical reasons). One example of these cooling experiments can be seen in *Figure 1*. The corresponding data of degree of transformation at a given temperature and cooling rate have been analysed according to the Ozawa equation which can be rearranged as follows:

$$\ln[-\ln(1-X_c)]=\ln k(T)+n\ln\left(\frac{1}{v}\right) \qquad (3)$$

The representation of this equation for PHD1 can be seen in *Figure 10*. It can be observed, as in the other two polymers, that relatively good straight lines are obtained, with approximately the same slope. The conclusion is, then, that the non-isothermal crystallization of these PHD samples can be analysed in terms of the Avrami equation and that similar mechanisms of nucleation and growth apply to all the temperatures and cooling rates in the ranges studied.

The Avrami exponent and the cooling function are obtained, respectively, from the slope and intercept of these straight lines. The corresponding values are listed in *Table 4*. It can be observed that the Avrami exponent seems to be around 4, i.e. a similar result to the isothermal experiments. The values of $\ln k(T)$ have been plotted in *Figure 11* as a function of temperature, finding a good fit to a straight line. This exponential dependence of the cooling function on temperature has been reported for other polymers[27–29].

CONCLUSIONS

Two d.s.c. peaks are found in both the melting and cooling of the three poly(1-hexadecene) samples with

Table 4 Parameters of the Ozawa equation for the non-isothermal crystallization of the isotactic content of the three poly(1-hexadecene) samples

T (°C)	Avrami exponent, *n* PHD1	PHD2	PHD3	ln *k*(*T*) PHD1	PHD2	PHD3
39			3.5			1.9
38.5	3.9		3.6	0.6		2.4
38	3.8		3.0	1.2		2.4
37.5	4.0	3.0	3.0	1.9	2.6	2.7
37	3.9	2.9	3.6	2.4	2.9	4.0
36.5	4.2	3.0	3.7	3.0	3.3	4.5
36		3.1	3.3		3.8	4.5
35.5	4.4	3.1	3.3	4.5	4.2	4.9
35		3.2	3.2		4.8	5.1
34.5	4.5	3.5		5.4	5.7	
34	4.4	3.5	2.8	6.0	6.2	5.2
33.5	4.4			6.5		
33	4.8	3.6		7.8	7.2	
32.5	4.8		3.2	8.3		7.0
32	4.7			8.7		
31.5		4.5			10.1	
31	4.6	4.6		9.0	10.7	
30.5		4.3	3.5		10.5	8.8
30		4.0			10.0	
29.5		4.2			10.8	
29		4.2			11.0	
28.5		4.2			11.5	
$\bar{n}$	4.3±0.3	3.7±0.6	3.3±0.3			

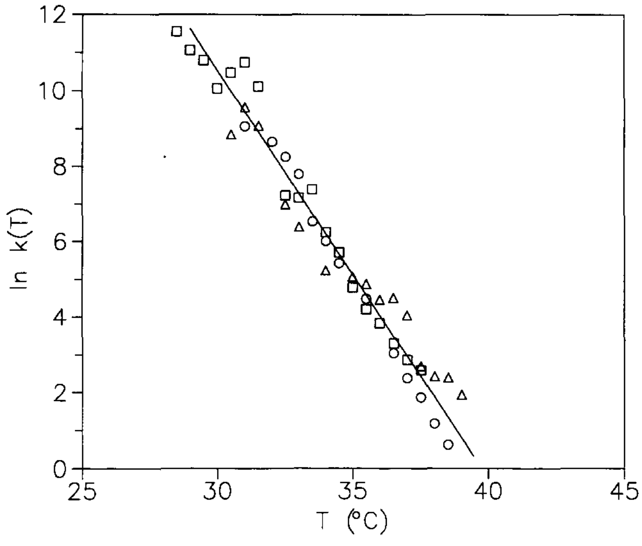

Figure 11 Variation of ln *k*(*T*) with temperature for the three poly(1-hexadecene) samples: (○) PHD1; (□) PHD2; (△) PHD3

different tacticity studied here. The high-temperature peak is attributed to the melting, or crystallization, of the crystallites of isotactic polymer and the lower-temperature peak to the atactic ones, i.e. there is a segregation of the two kinds of species.

Owing to overlapping problems, only the isothermal crystallization kinetics of the isotactic content can be studied. The corresponding analysis in the range of crystallization temperatures from 36 to 45°C showed that the process can be described by the Avrami equation up to relatively high conversions. The rate constant *k* of this equation increases very rapidly with undercooling, i.e. the overall rate of crystallization exhibits a negative temperature coefficient, indicating that the process is controlled by the nucleation. The value of the Avrami exponent is approximately 4, suggesting a homogeneous nucleation followed by three-dimensional growth.

The melting temperature of the isotactic content is independent of the crystallization temperature, as expected for this lateral crystallization where the crystal thickness is supposed to be constant and depends only in the number of carbons in the lateral branch. For the poly(1-hexadecene)s in this study, the value of T_m was found to be 58°C.

The study of the non-isothermal crystallization of PHDs shows that it can be analysed in terms of an Avrami-type equation and similar mechanisms of nucleation and growth apply to all temperatures and cooling rates in the ranges studied. Moreover, the Avrami exponent in this analysis is of the same order as in the case of the isothermal treatment.

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