Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 61–74

ANALYSIS OF THE DYNAMIC CRYSTALLISATION OF ISOTACTIC POLYPROPYLENE/α-NUCLEATING AGENT SYSTEMS BY DSC

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(Received October 31, 2001)

Abstract

The nucleation efficiency of dibenzylidene sorbitol, methyldibenzylidene sorbitol and 1,2,3,4-*bis*-(3,4-dimethylbenzylidene) sorbitol in the crystallisation of the monoclinic phase of isotactic polypropylene has been evaluated by differential scanning calorimetry as a function of cooling rate and nucleation agent concentration. In order to analyse the nucleation activity of the additives, the self-nucleation process of the pure polypropylene has also been studied by thermal techniques. A large increment in the crystallisation temperatures has been obtained even for the lowest additive concentration, and the nucleating efficiencies are of the highest observed for α-nucleating agents in isotactic polypropylene.

Keywords: crystallisation, DSC, efficiency, isotactic polypropylene, nucleating agents, sorbitol derivatives

Introduction

In semicrystalline polymers, both the mechanism and rate of crystallisation are fundamental parameters, since they control microstructural and morphological characteristics that ultimately determine the physical, optical and mechanical properties of these materials. A polymer crystallises when it is cooled to temperatures well below its melting temperature, and the subsequent solidification process can be described by a nucleation and growth mechanism. Nucleation corresponds to the initiation of the new crystalline phase and in general terms two types can be described. Homogeneous nucleation takes place at a constant rate and originates from statistical fluctuations of the polymer chains in the melt, whereas heterogeneous nucleation occurs at a variable rate and originates from the presence of a foreign phase in the polymer melt arising

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1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

from impurities, residual polymer crystals, or specific substances added to the system that may act as nucleating agents.

Isotactic polypropylene (iPP) can present four different crystalline polymorphs, α (monoclinic), β (hexagonal), γ (triclinic) and smectic [1–8], the α-form being the dominant polymorph encountered in the large majority of industrial applications of polypropylene crystallised under normal processing conditions. The crystallisation of iPP is controlled by the nucleation stage [9], and the addition of specific additives or nucleating agents to shorten the induction time of crystallisation and accelerate the formation of crystalline nuclei [10] is a technique commonly used in the polymer industry to shorten injection-moulding cycle times, thus reducing production costs. Furthermore, such agents generate smaller spherulites, thus improving the optical and mechanical properties [11]. In this respect, the control of the crystallisation rate from the melt provides an important method for the modification of the solid-state properties of the material, allowing the design of tailored materials for new applications.

A large number of compounds have been reported to nucleate the α form of iPP [10–14]. In order to evaluate the efficiency of a nucleating agent, an established method employed is to determine either the crystallisation temperature of the nucleated system in a dynamic DSC experiment, or the time needed to reach a given crystallisation transformation in an isothermal DSC experiment, and to compare them with the same parameter obtained for the polymer without additives. Fillon *et al.* [15, 16] determined this efficiency by considering the non-nucleated system as the lower limit, and a wholly self-nucleated polymer as the upper limit of the nucleation efficiency scale, reporting values for the most effective α-nucleating agents for iPP of between 50–66%.

In recent years there has been considerable interest in the development of transparent, high modulus materials based on polypropylene. Over the last decade, sorbitol and its derivatives have been widely used as agents to improve the transparency of iPP, the most representative examples being 1,2,3,4-dibenzylidene sorbitol, DBS, and 1,2,3,4-*bis*-(*p*-methoxybenzylidene sorbitol), DOS, considered as the first generation of sorbitol derivatives [17–21]. However, DBS has a nucleation efficiency of around 40%, and is far from the best performance level that would be expected for fully self-nucleated polypropylene. The second generation of sorbitol-based nucleating agents is comprised of alkyl and halo-derivatives, such as 1,2,3,4-*bis*-(*p*-methylbenzylidene sorbitol), MBDS, 1,2,3,4-*bis*-(*p*-ethylbenzylidene sorbitol), NC4, and 1,2,3,4-*p*-chloro-*p'*-methyldibenzylidene sorbitol [21]. More recently 1,2,3,4-*bis*-(3,4-dimethylbenzylidene sorbitol) has been developed as a representative of the third generation and most modern example of sorbitol-based nucleating agents for isotactic polypropylene.

This work presents a comparative study of the nucleating efficiency of the different sorbitol derivatives, benzylidene sorbitol, methyldibenzylidene sorbitol and 1,2,3,4-*bis*-(3,4-dimethylbenzylidene sorbitol) in the crystallisation process of the monoclinic phase of isotactic polypropylene. In order to determine the upper limit of the nucleation efficiency scale, the self-nucleation process in pure iPP has also been studied.

Experimental

Materials

iPP used in this study is a commercial grade supplied by Repsol-YPF with an isotacticity of 95% as determined by solution NMR and a viscosity average molecular mass, M_v of 164 700. The following nucleating agents were studied: Dibenzylidene sorbitol, 'Disorbene', from Roquette; two types of methyldibenzylidene sorbitol, 'Geniset MDG001' and 'Disorbene M', from NJC-Rika and Roquette, respectively; and 1,2,3,4-*bis*-(3,4-dimethylbenzylidene) sorbitol, 'Millad 3998', from Milliken Chemical. A series of compositions between 0.025–1.0% by mass of the nucleating agents in iPP were prepared by melt blending in a twin-screw laboratory extruder APV (MP 2030) at a rotor speed of 150 rpm. A compound of the nucleating agents and iPP powder obtained by cryogenic grinding was prepared beforehand, in order to incorporate such small concentrations of nucleating additives.

Physical properties

The thermal properties were analysed in a Perkin Elmer DSC-7/7700/Unix differential scanning calorimeter, calibrated with indium (T_m=156°C, ΔH_m=28.45 J g^{-1}). Crystallisation experiments were carried out under dynamic conditions both for pure iPP and the nucleated systems using the following experimental conditions: the samples were melted at 210°C for 10 min, and subsequently cooled to 40°C at cooling rates of 1, 2, 5, 10 and 20°C min^{-1}. The samples were then heated to 210°C at 10°C min^{-1} after crystallisation. All DSC experiments were carried out in a nitrogen atmosphere using 10 to 12 mg of sample sealed in an aluminium pan. The transition temperatures were taken as the peak minima in the crystallisation exotherms, and the degree of crystallinity was calculated from the ratio $\Delta H_a/\Delta H_u$, where ΔH_a and ΔH_u are the apparent enthalpy of crystallisation and that associated with 100% crystalline monoclinic polypropylene, 177.0 J g^{-1} [22].

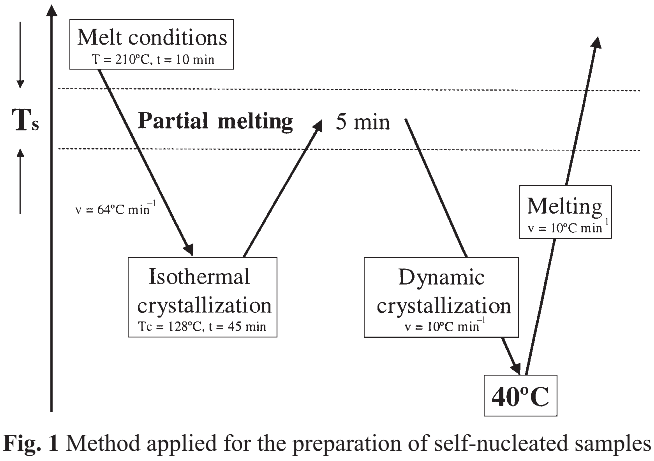

Fig. 1 Method applied for the preparation of self-nucleated samples

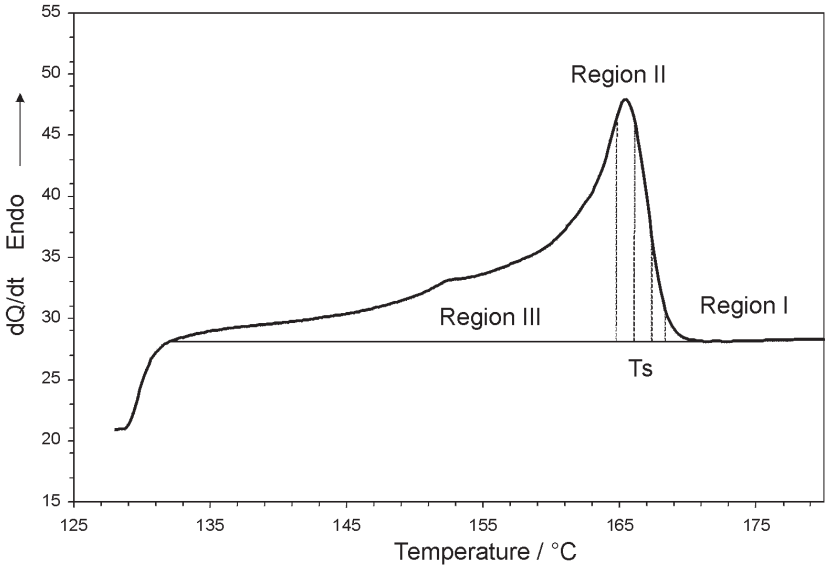

Fig. 2 DSC curve showing the location of the conditioning temperatures, T_s

The self-nucleation experiments for pure iPP were performed using four thermal steps, Fig. 1: a) the sample was held at 210°C during 10 min in order to eliminate the melt-phase memory effects, b) an isothermal crystallisation was executed at 128°C for 45 min, after cooling rapidly from the melt at 64°C min^{-1}, c) the samples were heated at 10°C min^{-1} to values of T_s selected between 175–160°C, Fig. 2, and maintained at these temperatures for five minutes. This is the essential step in self-nucleation, and d) dynamic crystallisation was carried out by cooling the samples to 40°C at 10°C min^{-1}. The subsequent heating process, at 10°C min^{-1} to 210°C, was also investigated.

Results and discussion

In the first instance, thermogravimetric analysis was undertaken in an oxygen atmosphere for all the materials. The initial degradation temperatures have been published elsewhere [23–25], and the thermal stabilities of the nucleated systems were found to be similar to that of pure iPP, indicating that blending does not affect the stability of the polypropylene matrix.

The crystallisation process depends not only on the molecular characteristics of the polymer, but also on the thermal history imposed. At the beginning of the crystallisation process, there are two types of nuclei present in the system. The heterogeneous nuclei formed by particles chemically different from the crystallising polymer are hardly affected by the thermal history of the melt. However, the concentration of athermal homogeneous nuclei, i.e. residual polymer crystal fragments left from previous structures, is very dependent on the melting temperature and melting time [26, 27]. For this reason, the influence of the melting conditions prior to crystallisation on the crystallisation rate was analysed and was described previously [23–25]. From these data, a temperature of 210°C and a residence time of 10 min were applied in all cases in order to erase any melt-phase memory of previous three-dimensional structure.

Moreover, prior to the study of the crystallisation behaviour of all the samples and the determination of the efficiency of the nucleating additives we have evaluated the self-nucleation of iPP used in this study, as this must be analysed for each particular sample [15]. Self-nucleation in polymers was first introduced by Blundell *et al.* [28] to describe the nucleation of chain folded crystals in solution by crystal fragments of high molecular mass present in the same solution. Nowadays, the term self-nucleation is generally applied to describe the nucleation of polymers in the melt or in solution induced by previously formed polymer crystals. Self-nucleation phenomena can be generated in DSC using four thermal steps, which correspond to [15, 16, 29]; a) Erasure of previous thermal history, b) creation of a crystalline state in predetermined dynamic or isothermal conditions, c) partial melting at a temperature located in the melting range, T_s, Fig. 2, and d) isothermal or dynamic crystallisation. The experimental conditions used to generate self-nucleation in this work were described in the experimental section.

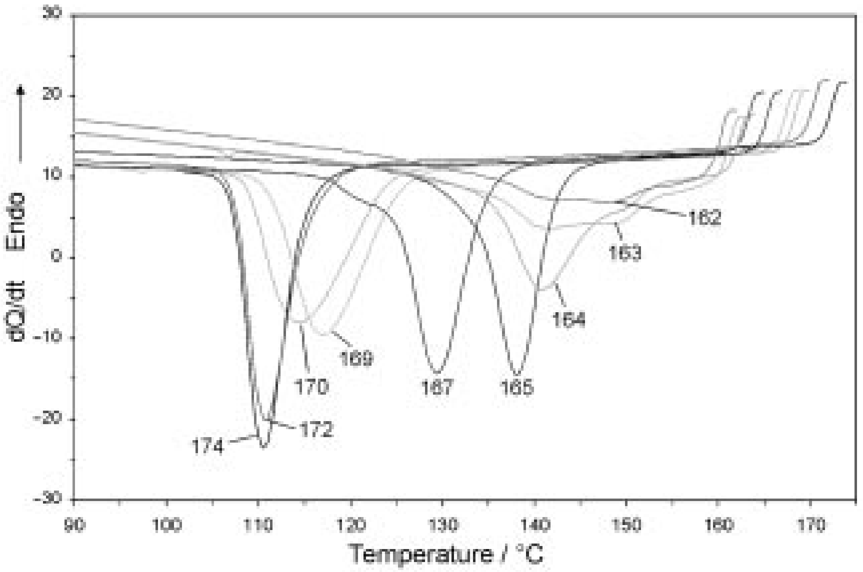

Fig. 3 Crystallisation exotherms of iPP cooled at 10°C min^{-1} after partial melting at indicated values of T_s

The dynamic crystallisation exotherms obtained after partial melting at different values of T_s are shown in Fig. 3. When T_s is located in the higher part of the melting range known as region II, between 165–170°C, a decrease in the crystallisation temperature is observed as T_s increases. This behaviour is related with a considerable decrease in the nucleation density as a consequence of the reduction in the concentration of residual crystallite fragments. On the other hand, when melting takes place at values of T_s above 170°C, region I, the number of nuclei remain at a minimal and constant level, and crystallisation occurs at the same temperature. When the sample is melted at values of T_s below 165°C, which corresponds to region III in the lower part of the melting endotherm, the crystallisation behaviour is complex. A double exotherm can be observed and shows a large reduction of the material that has recrystallized. It is clear that in this case the melting process is incomplete, and that only the smaller, more imperfect crystals melt whilst the others may undergo an annealing process during heating.

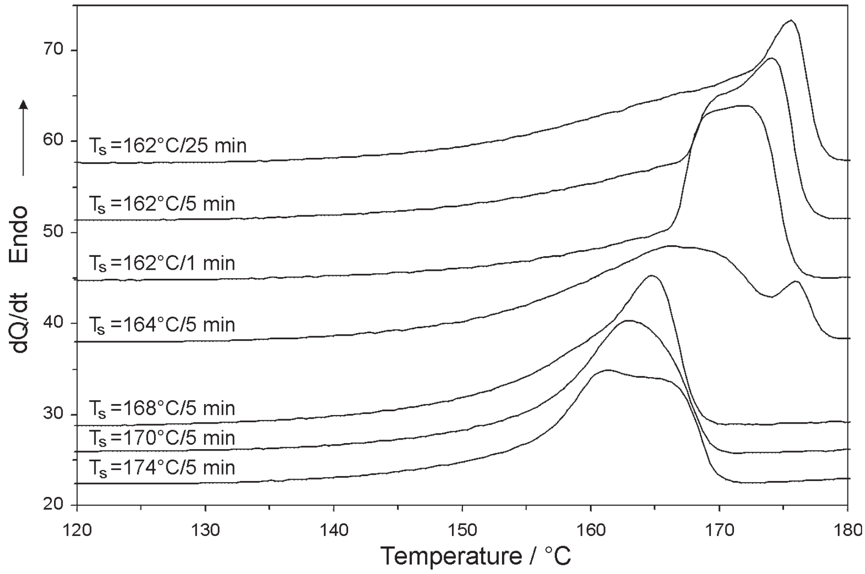

Fig. 4 Melting endotherms of iPP heated at 10°C min^{-1} after the recrystallization process in Fig. 1

Figure 4 shows the heating curves for the samples after the forementioned recrystallization process. In iPP samples which have been partially melted at values of T_s<165°C, two endothermic peaks are observed, one at high temperature (172–176°C) and the other at temperatures below 170°C. The low temperature peak arises from the melting of crystals formed during the cooling process. However, the higher temperature peak can be associated with those crystals which have not melted at T_s<165°C, and demonstrate an increase in their crystal sizes due to an annealing process on heating. When T_s increases within region III, the intensity of the higher temperature endotherm decreases because the concentration of crystals which may be annealed is smaller, however, the temperature of the peak is higher because the annealing takes place at high temperatures [15]. When the conditioning time at fixed T_s is increased, the temperature of the high temperature endotherm also increases confirming that an annealing process generates this endotherm. The double peak observed in both crystallisation and melting can be explained by modifications in the monoclinic structure of iPP that take place during the annealing process [30]. Two phases have been described, where phase α_1 is generated during the cooling process, and phase α_2 is that formed at high temperature with higher melting temperature, probably generated from the nuclei produced during the self-nucleation experiment. Clearly, the crystallisation temperature obtained during self-nucleation is totally dependent on the conditioning temperature, T_s, at which the partial melting has been performed. At T_s>170°C, a constant crystallisation temperature, T_c was obtained, considered as the crystallisation temperature of the non-nucleated iPP. For values of T_s in the interval between 165–170°C, a self-nucleation process occurs and the crystallisation temperature increases with T_s, reaching a maximum value of 140°C, temperature considered as the crystallisation temperature of the best self-nucleated sample. When T_s<165°C, the self-nucleation process competes with annealing, the latter becoming more important as the conditioning temperature and time increase.

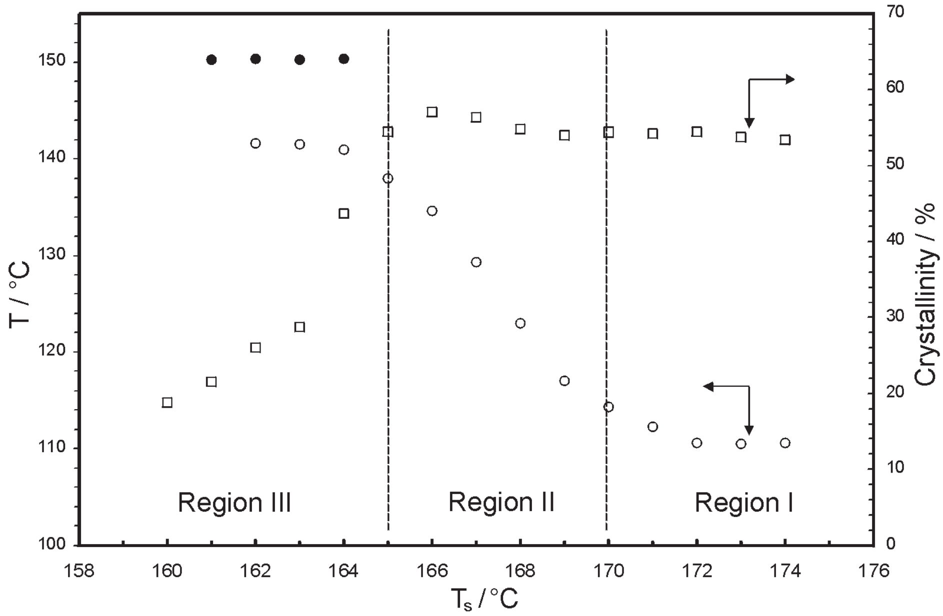

Fig. 5 Variation of o –, ● – crystallisation temperatures and □ – crystallinity obtained on cooling at 10°C min^{-1}, as a function of the partial melting temperature, T_s

The evolution of the crystallisation temperatures and their corresponding crystallinity values with T_s is shown in Fig. 5. In region I, the crystallisation temperatures and crystallinity are relatively constant. The crystals formed at the lowest

Table 1 Temperatures and enthalpies of crystallisation for nucleated and non-nucleated iPP at the indicated cooling rates

Agent	%	v_{20}		v_{10}		v_5		v_2		v_1	
		T_c	ΔH_c	T_c	ΔH_c	T_c	ΔH_c	T_c	ΔH_c	T_c	ΔH_c
–	0	104.9	89.3	110.1	93.5	113.2	94.8	117.9	95.5	121.2	93.5
Millad 3988	0.025	106.9	92.6	114.7	94.8	116.0	95.3	121.2	95.6	124.2	94.8
	0.05	109.4	93.2	116.1	95.2	118.9	96.8	123.3	96.2	127.0	97.5
	0.3	124.9	97.8	128.7	99.8	132.6	101.9	136.5	98.7	139.0	97.8
	0.5	126.1	97.5	129.6	100.2	133.6	100.9	137.5	101.3	138.7	102.3
	1.0	126.0	99.6	129.8	100.7	133.4	101.8	137.2	102.4	139.7	103.4
Geniset MDG001	0.1	106.0	91.7	115.4	95.5	119.0	95.4	123.3	99.6	122.8	98.4
	0.3	124.0	99.6	127.4	97.8	131.0	101.9	134.8	102.1	137.7	107.2
	0.5			128.0	100.3	131.2	100.3			137.9	102.7
Disorbene	0.05			114.0	94.8	117.9	94.2			125.5	102.2
	0.1			116.3	96.8	119.5	100.0			125.5	108.1
	0.2			121.7	98.3	124.8	102.0			130.0	110.5
	0.3			123.3	100.4	127.1	97.2			132.3	96.5
Disorbene M	0.05			113.3	97.1	117.2	99.9			124.8	100.0
	0.1			116.5	99.3	120.8	98.6			126.9	113.8
	0.2			128.7	100.1	131.9	102.7			138.3	107.2

v – cooling rate °C min^{-1}
T_c – crystallization temperature
ΔH_c – enthalpy of crystallisation

crystallisation temperatures are the smallest, and melt at very low temperatures, i.e. at 160°C. On heating, these imperfect crystals undergo a melting-recrystallization process that generates a second endotherm at 165–166°C, Fig. 4. In region II, the crystallisation temperatures increase and are accompanied by a slight increase in crystallinity when T_s decreases, as previously mentioned. Finally, in region III the crystallinity decreases with T_s, which correlates with the presence of the double endotherm due to a predominant annealing process instead of self-nucleation, as was seen in Fig. 4 and explained above.

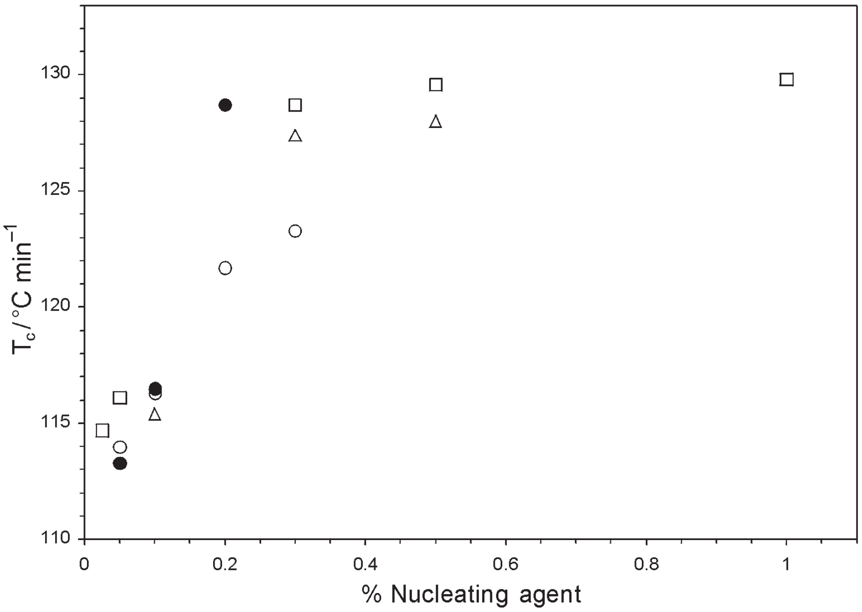

Fig. 6 Variation of crystallisation temperatures with concentration of nucleating agents for the cooling rate of 10°C min^{-1}, □ – Millad, Δ – Geniset MDG001, o – Disorbene, and • – Disorbene M

The crystallisation behaviour of the nucleated iPP systems was studied by DSC under dynamic conditions. The values of T_c and ΔH_c of nucleated iPP obtained at different cooling rates are given in Table 1. The crystallisation temperatures are observed to increase with increasing concentration of nucleating agent, and are highly dependent on the cooling rate. Figure 6 shows the differences in the crystallisation temperatures between iPP with different nucleating agents as a function of the concentration for a cooling rate v_c=10°C min^{-1}. It can be clearly observed that for all cases the crystallisation temperature increases relative to the value obtained for non-nucleated iPP. In the case of iPP nucleated with Millad 3988, an important increase in the crystallisation temperature can be observed with increasing nucleating agent concentration, particularly for lower levels up to around 0.3% [24]. The crystallisation temperature then tends to stabilize for higher concentrations, reaching a 20°C increase in T_c for 0.5% composition at a cooling rate of

10°C min^{-1}. Whereas, in the case of iPP nucleated with Geniset MDG001, the crystallisation temperature stabilises at a concentration of around 0.3%. The increase observed in the temperature of crystallisation up to concentrations of 0.1% Disorbene and Disorbene M is almost identical. However, for a concentration of 0.2%, the increase observed is significantly higher for Disorbene M, corresponding to a temperature of 128.7°C, compared to that of 121.7°C for Disorbene. Comparing both methyldibenzylidene sorbitols, Disorbene M seems to demonstrate a higher nucleating activity than Geniset MDG001.

The increase in the crystallisation rates induced by the nucleating agents is also reflected in the increase in the crystalline nucleation density, and the consequent increase in the concentration of crystalline entities produced, and correlates with a slight increase in the crystallisation enthalpy when the concentration of the nucleating agent is increased and the cooling rate reduced, Table 1. A maximum value of 64% is obtained for the crystallinity of the nucleated systems compared to 53% for the non-nucleated iPP at a cooling rate of 1°C min^{-1}. Generally speaking, for a cooling rate of 10°C min^{-1} an increase of 3–4% in crystallinity has been obtained by nucleation; clearly far less significant than the increase observed in the crystallisation temperature, as can be seen in Fig. 7. This increase in the level of crystallinity results in a loss of flexibility of the material and, as a consequence, an increase in the flexural modulus and variations in the optical properties, as is described elsewhere [25].

The nucleation efficiency, *NE* can be represented by comparing the crystallisation performance of the nucleated system with that of self-nucleation of the matrix polymer due to the presence of pure iPP crystallites, considered as the best possible

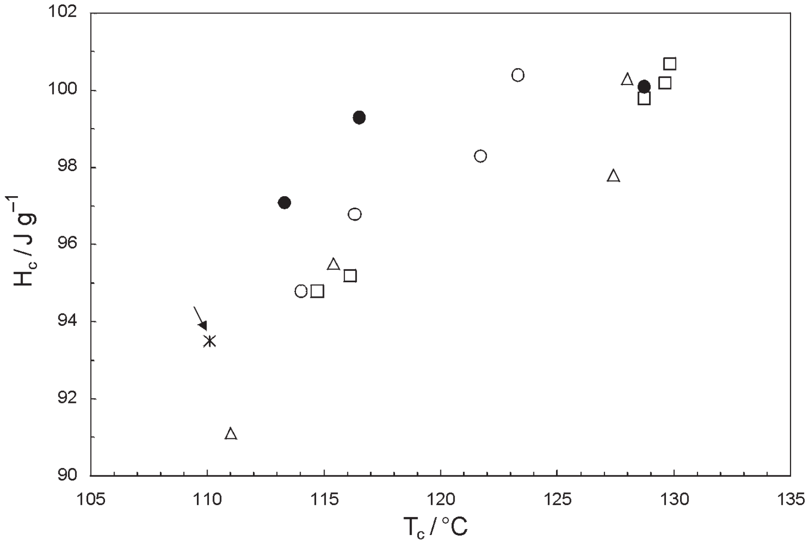

Fig. 7 Variation in the enthalpy of crystallisation with the crystallisation temperature for the following nucleating agents: □ – Millad 3988, Δ – Geniset MDG001, o – Disorben and • – Disorbene M, cooling rate=10 °C min^{-1}. ∗ – value for PP without nucleating agent

efficiency, since the concentration and distribution and the interactions between the nucleating agent and the matrix are ideal [15, 16, 20, 21, 28]. The non-nucleated sample and the best self-nucleated sample are considered as the two extreme limits of the efficiency scale for a particular polymer. Thus, *NE* varies from 0 to 100 and can be given by the following expression,

$$NE=100(T_c-T_{c1})/(T_{c2max}-T_{c1}) \quad (1)$$

where T_{c1} and T_{c2max} are the crystallisation temperatures of the non-nucleated and the self-nucleated polymer, respectively [21]. A value of 140°C was used for T_{c2max} obtained from the self-nucleation experiments.

The evolution of the nucleating efficiency as a function of nucleating agent concentration is represented in Fig. 8 for different nucleating agents. In the case of the sorbitol derivatives Millad 3988 and Geniset MDG001, the efficiency reaches values of between 60–65%, clearly well above those described in the literature for DBS (around 40%) for the same concentration levels, although in all cases the values are far removed from the ideal case of the self-nucleated iPP. It is clear that the dibenzylidene sorbitol Disorbene presents the lowest nucleation efficiency, of between 40–42% for the same levels of concentration. On the other hand, the more highly substituted sorbitol derivatives seem to present an almost uniform nucleation efficiency, of between 55–65% for concentrations higher than 0.2% of nucleating agent.

In order to more clearly illustrate these results, Fig. 9 shows *NE* values obtained, and compares them with values given in literature for a series of sorbitol derivatives with different aromatic and aliphatic substitution, crystallised in an analogous man-

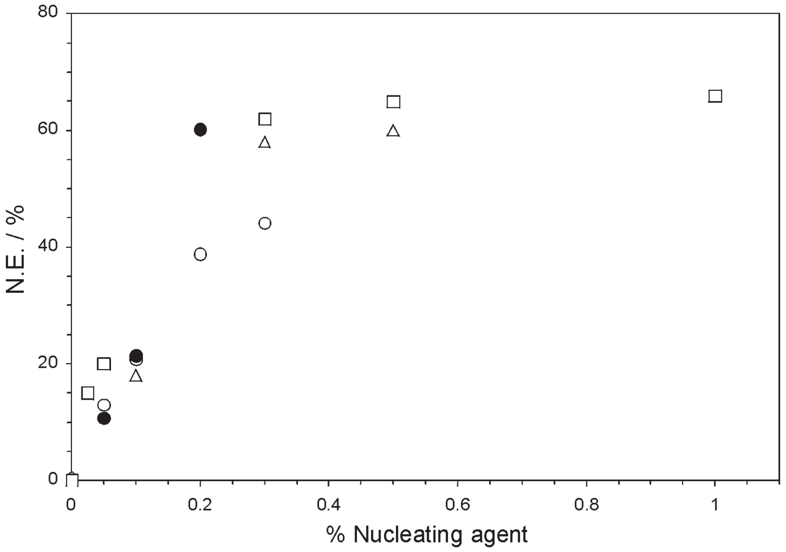

Fig. 8 Variation in the nucleating efficiency as a function of composition for the following nucleating agents; □ – Millad 3988, Δ – Geniset MDG001, o – Disorbene and ● – Disorbene M, cooling rate=10 °C min^{-1}

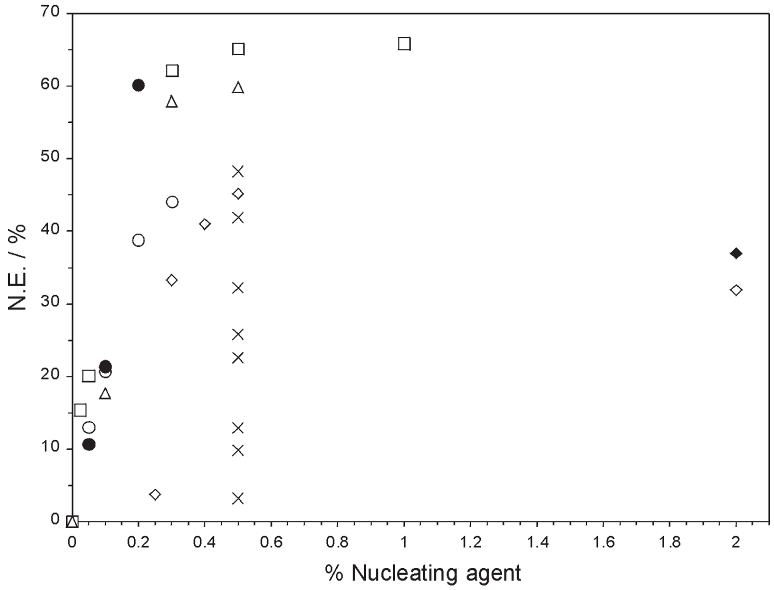

Fig. 9 Comparison of the nucleation efficiency of the nucleating agents in this work with results for sorbitol derivatives described in the literature; □ – Millad 3988, Δ – Geniset MDG001, o – Disorbene, ● – Disorbene M, ✧ – DBS [20, 21, 31–34], ◆ – EDBS [32] and × – other sorbitol derivatives [33]

ner [20, 21, 31–34]. It can be observed that for similar concentrations of nucleating agent, the results obtained for Millad 3988 and Geniset MDG001 demonstrate higher nucleation efficiency [24]. It is also significant that the nucleation efficiency in the case of Disorbene is higher than that observed for other DBS systems, over the same concentration range, between 0.2–0.3%, and also at much higher concentrations such as 2% [20, 21, 31–34], which could be related to a higher level of dispersion of the DBS, Disorbene in the polypropylene matrix.

Although it was previously explained that the nature of the nucleating agent plays a fundamental role in the nucleation efficiency represented by the crystallisation temperature, the dependence of the crystallisation enthalpy, and consequently the crystallinity, on the crystallisation temperature, as a function of the type and composition of the nucleating agent has been found to be very similar in all cases [23–25]. It is well known that, as well as depending on the level of dispersion of the nucleating agent, the heterogeneous nucleation of isotactic polypropylene in these systems is controlled by the interactions that take place between the polymer and the nucleating agent [12, 32, 35–38]. The mechanisms by which they act are still relatively unknown, however a variety of studies have suggested a series of structural factors in the nucleating additives based on sorbitol derivatives, such as hydrogen bonding and dimerisation [17], van der Waals interactions [38], stereo isomerism [33], etc.

Finally, the melting behaviour of all the nucleated systems was also investigated. The heating of samples crystallised under dynamic conditions at different cooling rates showed two endotherms for non-nucleated iPP with peak maximums highly dependent on cooling and heating rates. However, in the nucleated systems the endotherm at lower temperature is hardly observable, and the endotherm at high temperature is observed in the range between 164–170°C. This behaviour will be analysed and presented elsewhere [39], but is important to point out here that whilst the nucleating agents increase the crystallisation temperature, they reduce the tendency of the crystals to recrystallize in the melting process, which is an indication of a higher stability of the polymer crystals formed.

Conclusions

The control of the crystallisation process by the careful selection of nucleating additives is of great interest to the polypropylene industry, for its implications in the development of new materials based on iPP. The nucleation efficiency of a series of sorbitol derivatives in the crystallisation of the monoclinic phase of iPP has been studied by DSC. In order to compare this parameter for different systems, it is essential to consider autonucleation phenomena in the iPP matrix, and to carefully control the thermal history of the materials. Taking into account these factors, the improvement in the efficiency of 2nd and 3rd generation sorbitol derivatives over DBS is significant and, in general terms can be classified in the following manner; 1,2,3,4-*bis*-(3,4-dimethylbenzylidene sorbitol)>methyldibenzylidene sorbitols> dibenzylidene sorbitol. It has been demonstrated that nucleation efficiencies of between 60–65% can be achieved for additive concentrations of between 0.2–1.0%, and that in the specific case of the methyldibenzylidene sorbitol Disorbene M, an efficiency of over 60% at a concentration of 0.2% was observed. These values are amongst the highest obtained for α nucleating agents of iPP.

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The authors wish to thank C. Blancas (REPSOL-YPF), M. A. Lopéz Galán (ICTP) and M. García (ICTP) for their collaboration. Financial support from the following research projects is gratefully acknowledged: CICYT-MAT98-0914 and CAM-07N/0032/1999.

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