

# Comparative Study of the Nucleation Activity of Third-Generation Sorbitol-Based Nucleating Agents for Isotactic Polypropylene

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Received 26 April 2001; accepted 15 September 2001

Published online 15 April 2002 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/app.10533

**ABSTRACT:** The nucleation activity of the sorbitol derivatives 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol) and methylidibenzylidene sorbitol are compared with that of talc, a conventional nucleating agent for the monoclinic crystalline phase of isotactic polypropylene. The thermal parameters associated with the dynamic crystallization process are studied as a function of the cooling rate by differential scanning calorimetry, and the nucleating efficiency is assessed by comparison with self-nucleation, the highest values being observed for 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol) over the whole concentration range. The nature of the polymer crystals formed in the nucleated polymer was studied by X-ray diffraction, and the data show an increase in a preferred orientation of the polymer crystallites with increasing concentration of nucleating agent. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2440–2450, 2002

**Key words:** polypropylene; nucleation; crystallization; differential scanning calorimetry

## INTRODUCTION

The properties of semicrystalline polymers depend to a large extent on both morphological and microstructural characteristics, which are controlled by the mechanism and rate of crystallization of the material. Isotactic polypropylene provides an example of the complex nature of crystallization, presenting four different crystalline

polymorphs,  $\alpha$  (monoclinic),  $\beta$  (hexagonal),  $\gamma$  (triclinic), and smectic,<sup>1–8</sup> but with identical chain conformation, corresponding to a  $3_1$  helix (tgtg). In the  $\alpha$ -form, the isotactic polypropylene (iPP) chains are arranged parallel in a monoclinic unit cell with a fiber axis of 6.5 Å and alternate between layers of right-handed and left-handed helices.<sup>3,4</sup> This polymorph is the most stable thermodynamically and dominant in the crystallization of iPP under normal processing conditions and is encountered in the majority of industrial applications of polypropylene.

The crystallization of iPP is controlled by the nucleation stage,<sup>9</sup> and in the high temperature region where heterogeneous nucleation is predominant, the formation of crystalline nuclei can

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Contract grant sponsor: CICYT; contract grant number: MAT98-0914; contract grant sponsor: CAM; contract grant number: 07N/0032/1999.

*Journal of Applied Polymer Science*, Vol. 84, 2440–2450 (2002)  
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be accelerated by the presence of discrete particles that act as foreign nuclei in the polymer melt.<sup>10–14</sup> These particles act as nucleating agents by reducing the induction time for crystallization, because the polymer melt does not need to form its own nuclei to initiate the crystallization process. They provide surfaces or nuclei that reduce the free energy barrier of the process,<sup>10</sup> modify the size and density of the spherulites formed, and, consequently, alter the optical and mechanical properties of the material. In this respect, the control of the crystallization rate from the melt provides an important method for the modification of the solid-state properties of the material, allowing the design of materials for new applications. Furthermore, by using nucleating agents, the cycle times can be considerably reduced, especially in injection molding, which can have a decisive influence on the processing costs.

Sorbitol and its derivatives have been used during the last decade as agents to improve the transparency of iPP. The most representative example is 1,2,3,4-dibenzylidene sorbitol (DBS), which along with 1,2,3,4-bis(*p*-methoxybenzylidene sorbitol) (DOS), encompasses the first generation of sorbitol derivatives.<sup>15–19</sup> The second generation of sorbitol-based nucleating agents comprises its alkyl and haloderivatives, such as 1,2,3,4-bis(*p*-methylbenzylidene sorbitol) (MBDS), 1,2,3,4-bis(*p*-ethylbenzylidene sorbitol) (EDBS), and 1,2,3,4-*p*-chloro-*p*'-methyldibenzylidene sorbitol.<sup>20</sup> More recently, 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol) was developed as a representative of the third generation and most modern example of sorbitol-based nucleating agents for iPP.

In this article, the nucleating activity of the sorbitol derivatives methyldibenzylidene sorbitol and 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol), compared with talc as a conventional  $\alpha$ -nucleating agent for iPP, is discussed on the basis of results from differential scanning calorimetry (DSC), using as a parameter of evaluation the crystallization temperature as a function of the cooling rate, with the object of developing polypropylene materials with high modulus and transparency.

## EXPERIMENTAL

### Materials and Sample Preparation

A commercial-grade polypropylene with a viscosity-average molecular weight,  $M_v$ , of 164,700 was

supplied by REPSOL-YPF (Madrid, Spain) and has been described in a previous study.<sup>21</sup> The nucleating agents used were methyldibenzylidene sorbitol, GENISET MDG001 (from NJC-RIKA, Osaka, Japan), 1,2,3,4-bis(3,4-dimethylbenzylidene sorbitol), MILLAD 3988 (from Milliken Chemical, Gent, Belgium), and talc, STEAMIC 00S (from Luzenac, Toulouse, France).

A series of compositions between 0.025 and 1.5 wt % of the nucleating agents in iPP were prepared by melt blending in a twin-screw laboratory extruder by using the conditions previously described.<sup>21</sup>

### Physical Properties

The thermal stability was studied by using a Mettler TA-4000/TG-50 thermobalance in an oxygen atmosphere at a flow rate of 150 mL min<sup>-1</sup> and a heating rate of 20°C min<sup>-1</sup>. The characteristic temperatures corresponding with the start of weight loss,  $T_i$ , and 10% weight loss,  $T_{10}$ , were determined from the thermogravimetric curves, both in the case of the pure nucleating agents and in the iPP/nucleating agent systems.

Dynamic DSC was undertaken in a Perkin-Elmer DSC-7-7700, calibrated with indium ( $T_m = 156^\circ\text{C}$ ,  $\Delta H_m = 28.45 \text{ J g}^{-1}$ ), and the data were evaluated by using the DSC-7/UNIX program. The experiments were carried out in an inert nitrogen atmosphere by using 10–12 mg of sample sealed in an aluminum pan. Crystallization experiments under dynamic conditions were carried out both for pure iPP and for the nucleated systems by cooling to 40°C, after melting the samples at 210°C for 10 min, at cooling rates of 1, 2, 5, 10, and 20°C min<sup>-1</sup>. All samples were heated to 210°C at 10°C min<sup>-1</sup> after crystallization. The crystallization temperature,  $T_c$ , was that corresponding to the peak minimum in the crystallization exotherm.

The apparent transition enthalpy,  $\Delta H_a$ , was determined as the area below the transformation curve, taking as the upper and lower limits the corresponding deviations in the baseline. The conversion corresponding to  $\Delta H_a$ , both in the melting and in the crystallization processes, is given as values of crystallinity,  $1 - \lambda$ , by

$$1 - \lambda = \Delta H_a / \Delta H_u \quad (1)$$

where  $\Delta H_a$  is the enthalpy of crystallization, determined by integration of the corresponding DSC exotherm, and  $\Delta H_u$  is the enthalpy associated

**Table I** Temperatures of Thermal Decomposition in an Oxygen Atmosphere at a Heating Rate of 20°C min<sup>-1</sup>

Matrix or Nucleating Agent	% Wt	$T_i$ (°C)	$T_{10}$ (°C)
IPP	—	225	255
MILLAD 3988	—	265	—
GENISET MDG001	—	256	—
STEAMIC 00S	—	260	—
MILLAD 3988	0,025	226	261
	0,05	224	257
	0,3	223	254
	0,5	227	260
	1	226	263
GENISET MDG001	0,1	226	260
	0,3	224	259
	0,5	228	258
STEAMIC 00S	0,5	225	258
	1	225	260
	1,5	226	259

with 100% crystalline monoclinic polypropylene, with a value of 177.0 J g<sup>-1</sup>.<sup>22</sup>

Wide-angle X-ray diffraction (WAXS) measurements were obtained by using a Rigaku Geigerflex-D/max X-ray diffractometer fitted with a Rigaku RU-200 12 kW rotating anode generator on films obtained by compression molding with thermal histories identical to those investigated by DSC. The diffractograms were recorded by using Ni-filtered CuK $\alpha$  radiation with a wavelength of 1.5418 Å, in the 2 $\theta$  range from 5 to 35° at a scanning rate of at 1°C min<sup>-1</sup>.

## RESULTS AND DISCUSSION

### Thermal Stability

To confirm the thermal stability during the different thermal cycles applied in the analysis of crystallization and melting, thermogravimetric analysis in oxygen was undertaken for all the materials, including the nucleating agents. This type of atmosphere is much more aggressive than the inert nitrogen environment in which all the DSC experiments were executed. The values of  $T_i$  and  $T_{10}$  obtained under the conditions described in the experimental section for each individual material, and for the nucleated samples of iPP, are given in Table I. In all cases, the initiation of thermal decomposition of the nucleating agents is far removed from that of the conditioning temper-

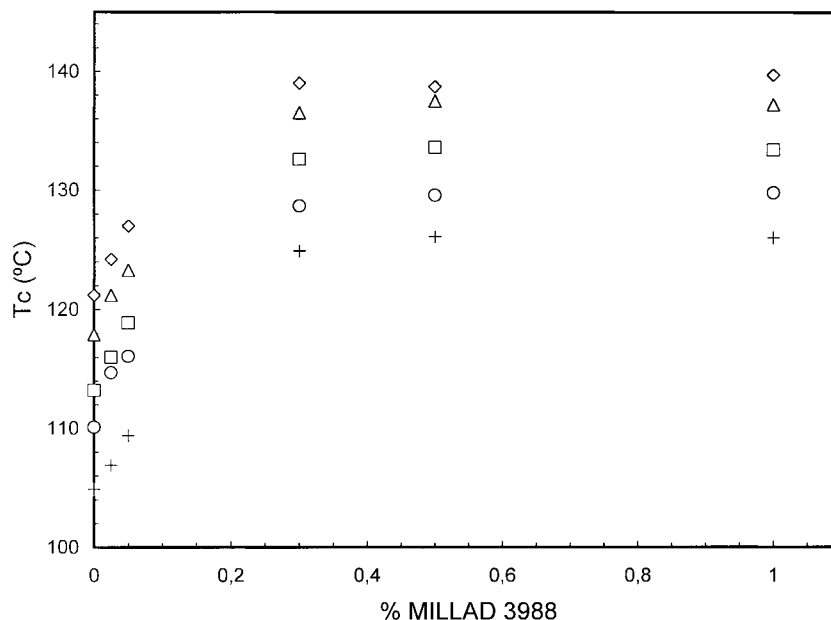
ature in the melt of 210°C at which all the samples were held prior to crystallization. On the other hand, the nucleated iPP samples show a thermal stability similar to that of pure iPP, which indicates that the method of preparation does not affect the thermal stability of the polypropylene matrix.

### Crystallization Behavior

The crystallization process is a first-order transition that takes place when the polymeric material is cooled from the molten state to a temperature range located between the glass transition temperature and the melting temperature, at relatively large undercoolings, and is due to the formation of crystalline nuclei and their subsequent growth. In homogeneous nucleation, stable crystalline nuclei are generated by the existence of statistical fluctuations in the melt, and the nucleation rate is constant. In the case of heterogeneous nucleation, the rate is variable, because it is the presence of heterogeneities in the system that induces the development of crystalline material. In any case, the nuclei present in the system at the start of the crystallization process include heterogeneous nuclei formed by particles chemically different from the crystallizable polymer, such as catalysts, pigments, impurities, nucleating agents, and the homogeneous or athermal nuclei.

Given that the rate of crystallization depends on the thermal history, melt-phase memory effects must be considered when studying polymer crystallization. In this regard, although the role of the heterogeneous nuclei can be regarded as surface defects and as such practically insensitive to the thermal history of the melt, the concentration of athermal nuclei (i.e., preexisting crystallite structures in the melt), with the same chemical structure as the matrix, is strongly conditioned by the melting temperature and the residence time at that temperature in the molten phase.<sup>23,24</sup> For this reason, and to select the thermal history prior to crystallization required for good reproducibility of the crystallization process, in earlier work<sup>21</sup> the influence of the melting conditions prior to crystallization on the crystallization rate was analyzed, and the temperature of 210°C and a residence time of 10 min were determined to erase any melt-phase memory of the previous three-dimensional structure.

Figure 1 shows the evolution of the crystallization temperature for nucleated iPP with the com-



**Figure 1** Variation of crystallization temperatures with concentration of MILLAD 3988 at the following cooling rates:  $20^{\circ}\text{C min}^{-1}$  (+);  $10^{\circ}\text{C min}^{-1}$  (○);  $5^{\circ}\text{C min}^{-1}$  (□);  $2^{\circ}\text{C min}^{-1}$  (△); and  $1^{\circ}\text{C min}^{-1}$  (◇).

position of MILLAD 3988 where, at all the cooling rates employed, an important increase in the crystallization can be observed with increasing nucleating agent content principally in the low concentration region, up to values of around 0.3% MILLAD 3988. The crystallization temperature then tends to level out for higher concentrations of nucleating agent, reaching an increase of around  $20^{\circ}\text{C}$  for the 0.5% composition at a cooling rate of  $10^{\circ}\text{C min}^{-1}$ . In this respect, an increase in the crystallization enthalpy with composition is also seen (Fig. 2), which is especially sensitive up to compositions of 0.3% MILLAD 3988, reaching values of around  $103\text{ J g}^{-1}$ , for the sample with 1% MILLAD 3988 crystallized at  $1^{\circ}\text{C min}^{-1}$ , which corresponds to a crystallinity of 58% when compared with the value of 54% obtained for pure iPP crystallized under the same conditions. In the case of iPP nucleated with the agent GENISET MDG001, the crystallization temperature stabilized at a concentration of around 0.3% (Fig.3), reaching crystallinity values similar to those obtained for MILLAD 3988. In the case of STEAMIC 00S, higher values of composition were used and an increase in the crystallization temperature of between 11 and  $13^{\circ}\text{C}$  was achieved for compositions of 0.5 and 1.5%, respectively, as can be seen in Figure 4.

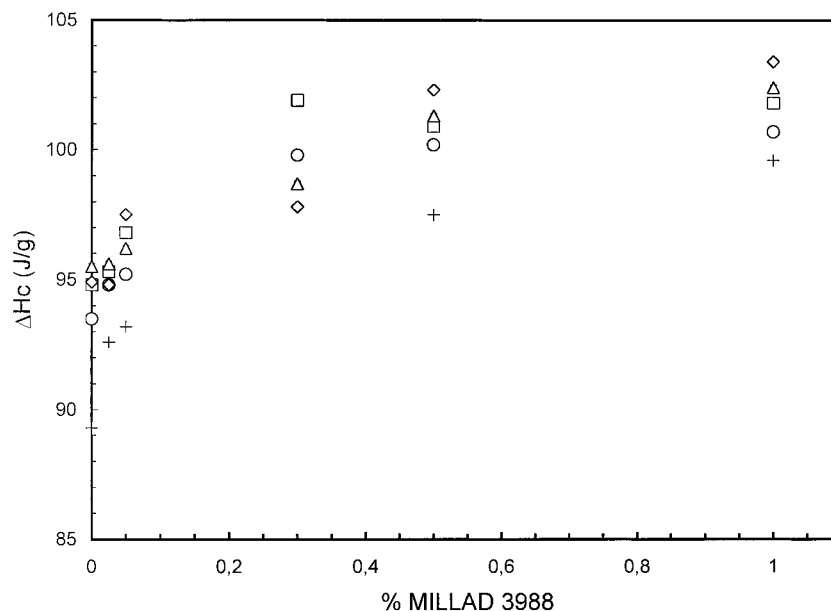
In all cases, the increase in the crystallization temperature appears to stabilize at higher con-

centrations of nucleating agent, above 0.3%, and the lowest nucleating activity is that achieved with STEAMIC 00S. The nucleation efficiency, NE, can be represented by a methodology based on the comparison with the self-nucleation of the matrix polymer due to the presence of pure iPP crystallites, because the concentration, the distribution, and the interactions between the nucleating agent and the matrix are ideal<sup>18,19,25–27</sup> and can be described by

$$\text{NE} = 100(T_c - T_{c1}) / (T_{c2\text{max}} - T_{c1}) \quad (2)$$

where  $T_{c2\text{max}}$  and  $T_{c1}$  are the crystallization temperatures associated with self-nucleated and non-nucleated iPP.<sup>19</sup>

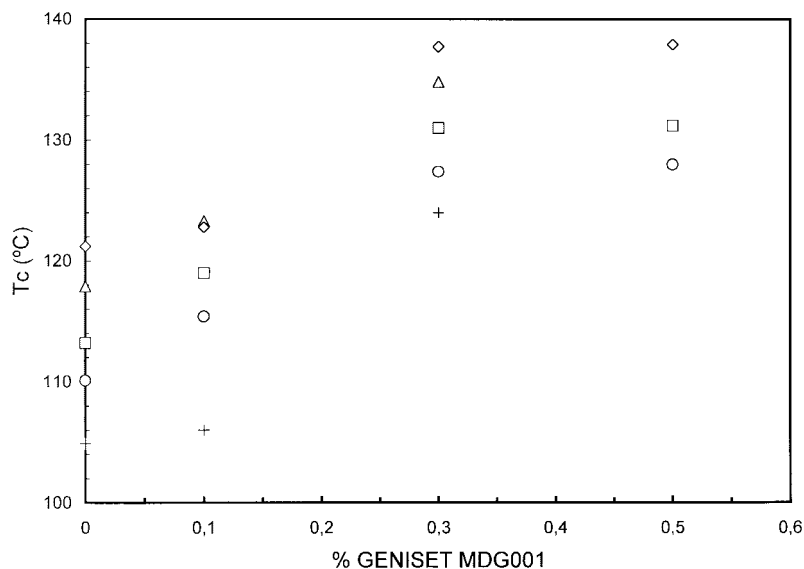
Taking into account the same cooling rate of  $10^{\circ}\text{C min}^{-1}$ , and a value of  $T_{c2\text{max}}$  of  $140^{\circ}\text{C}$ ,<sup>21</sup> Figure 5 shows the comparative evolution of the nucleating efficiency as a function of nucleating agent concentration. For concentrations  $\geq 0.3\%$ , STEAMIC 00S shows the lowest efficiency between 35 and 40%, whereas in the case of the sorbitol derivatives MILLAD 3988 and GENISET MDG001, the efficiency reaches values of between 60 and 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.



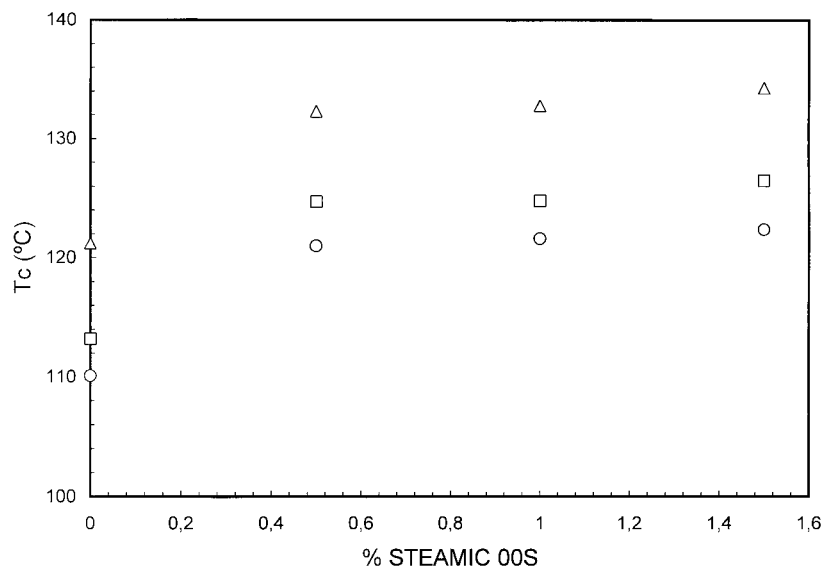
**Figure 2** Variation in the crystallization enthalpy with concentration of MILLAD 3988 at the following cooling rates: 20°C min<sup>-1</sup> (+); 10°C min<sup>-1</sup> (○); 5°C min<sup>-1</sup> (□); 2°C min<sup>-1</sup> (△); and 1°C min<sup>-1</sup> (◇).

Heterogeneous nucleation is based on the fact that the interfacial free energy of the embryo crystallite is reduced because of the presence of a foreign phase, that of the nucleating agent, which provides part of the crystalline interface. This leads to a reduction in the free energy of activation, and consequently, a reduction in the under-

cooling required for the nucleation process. Although it was previously explained that the nature of the nucleating agent plays a fundamental role in the nucleation efficiency represented by the crystallization temperature, the dependence of the crystallization enthalpy, and consequently the crystallinity, on the crystallization tempera-



**Figure 3** Variation in the crystallization temperatures with concentration of GENISET MDG001 at the following cooling rates: 20°C min<sup>-1</sup> (+); 10°C min<sup>-1</sup> (○); 5°C min<sup>-1</sup> (□); 2°C min<sup>-1</sup> (△); and 1°C min<sup>-1</sup> (◇).

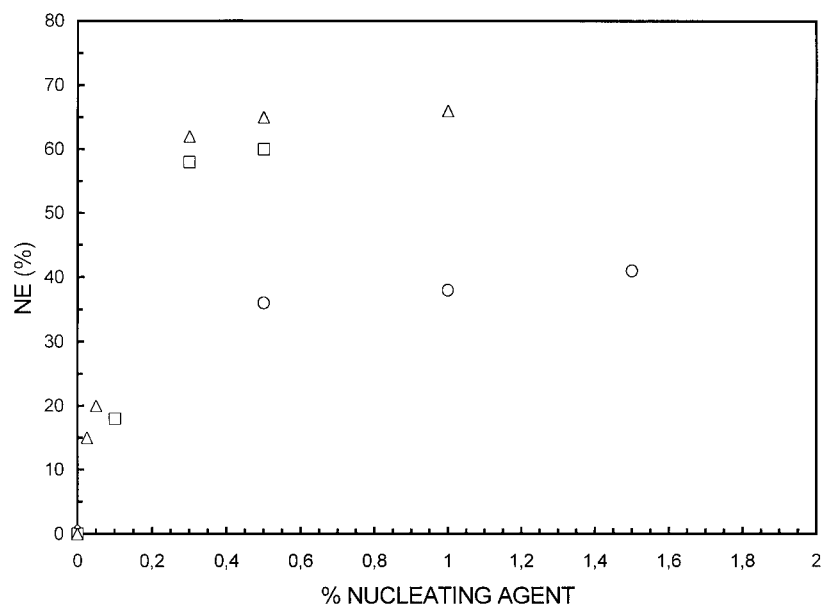


**Figure 4** Variation in the crystallization temperatures with concentration of STEAMIC 00S at the following cooling rates: 10°C min<sup>-1</sup> (○); 5°C min<sup>-1</sup> (□); and 1°C min<sup>-1</sup> (△).

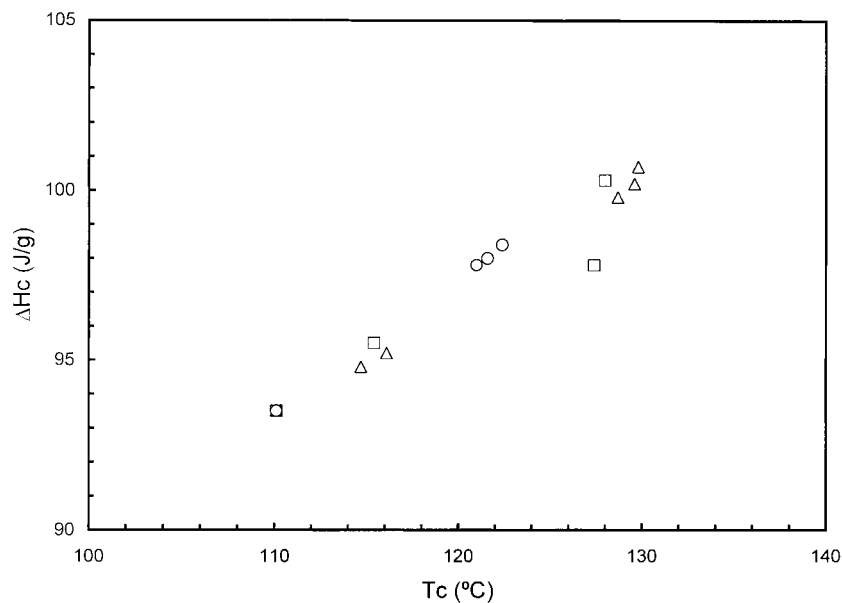
ture, as a function of the type and composition of the nucleating agent was very similar in all cases, as can be observed in Figure 6, in agreement with some observations described in the literature.<sup>28</sup> This increase in the level of crystallinity results in a loss of flexibility of the material, and as a consequence, an increase in the flexural modulus

and the optical properties, as will be described elsewhere.<sup>29</sup>

The WAXS data obtained at room temperature after dynamic crystallization at the indicated cooling rates showed in all cases the formation of the  $\alpha$ -crystalline modification (monoclinic) of iPP, with characteristic reflections at the following an-



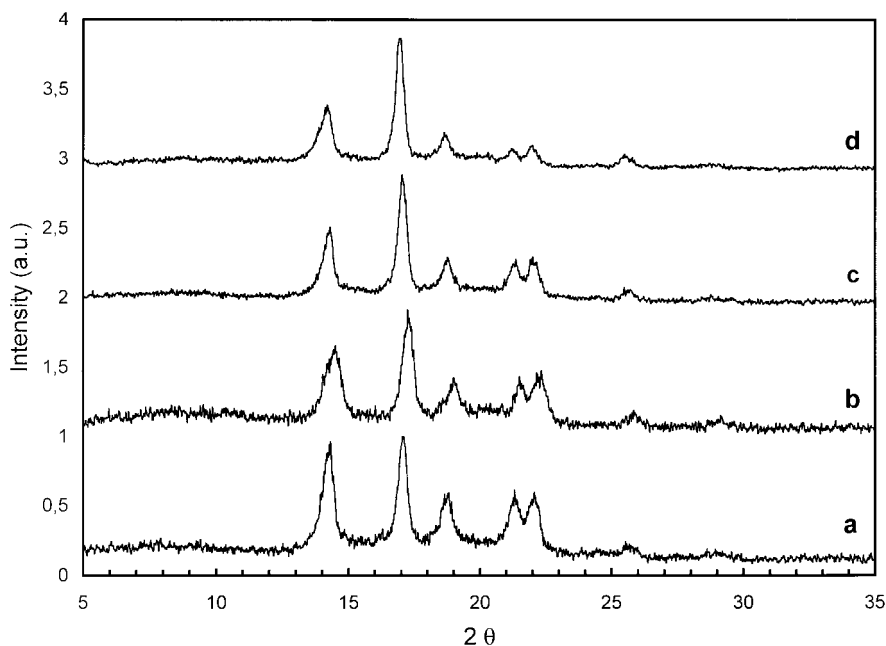
**Figure 5** Variation in the nucleating efficiency as a function of composition for the following nucleating agents: STEAMIC 00S (○); GENISET MDG001 (□); and MILLAD 3988 (△).



**Figure 6** Variation in the enthalpy of crystallization with the crystallization temperature for the following nucleating agents: STEAMIC 00S (○); GENISET MDG001 (□); and MILLAD 3988 (△) (Cooling rate =  $10^{\circ}\text{C min}^{-1}$ ).

gles,  $2\theta = 14.2^{\circ}$ ,  $17.0^{\circ}$ ,  $18.8^{\circ}$ ,  $21.2^{\circ}$ , and  $22.0^{\circ}$ , corresponding to the following crystalline planes (110), (040), (130), (111), and (041), respectively. No evidence of the  $\beta$ -crystalline modification was

observed. The analysis of the preliminary WAXS results point toward the existence of a series of phenomena directly related to the unit cell of the nucleated polypropylene. In Figure 7, which com-



**Figure 7** WAXS diffractograms registered at room temperature of (a) pure iPP, and iPP nucleated with MILLAD 3988 at the following concentrations: (b) 0.05%; (c) 0.3%; and (d) 1%.

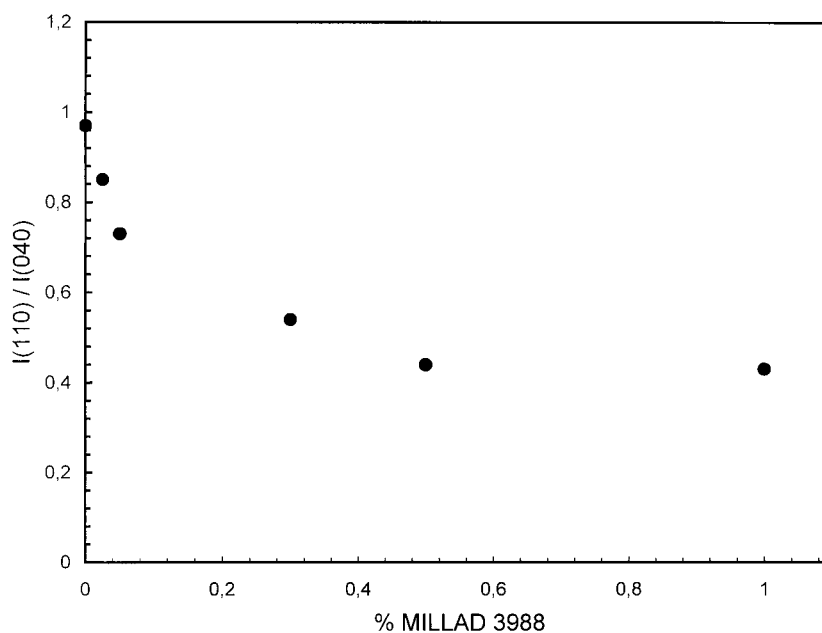


compares the diffractograms of pure iPP and that nucleated with MILLAD 3988, the most significant observations are the reduction in the intensity of the reflections associated with the (110), (130), (111), and (041) planes with increasing nucleating agent concentration. The ratio between the intensities of the (110) and (040) reflections provides information on the relationship between the orientation of the a and b axes in the monoclinic unit cell of polypropylene.<sup>30</sup> Figure 8 represents this ratio as a function of the concentration of MILLAD 3988, which clearly diminishes with increasing concentration of nucleating agent. This effect may be associated with an increase in the orientation of the b-axis<sup>31</sup> due to the presence of the nucleating agent, indicating that during crystallization the growth along the b-axis is relatively favored, although this is not the preferred growth direction in isotactic polypropylene. Although it is evident that the displacement of the crystallization range to higher temperatures improves the stability of the polymeric crystals, this fact is not necessarily related to the variations in the structural parameters observed by X-ray diffraction.

To analyze the influence of the presence of two nucleating agents of the  $\alpha$ -modification on the dynamic crystallization behavior of iPP, a sample was prepared with 1.5% STEAMIC 00S and 0.5% MILLAD 3988. In Table II, the tem-

perature and enthalpy of crystallization corresponding to this binucleating compound is compared with the mononucleating action of both agents at similar concentrations. In the binucleated iPP sample, no synergic effects are observed. On the contrary, at cooling rates of 5 and 10°C min<sup>-1</sup>, the values of the crystallization temperature are very similar to those corresponding to the iPP system nucleated with 0.5% MILLAD 3988, and higher than those corresponding to the iPP system nucleated with 1.5% talc. However, at a cooling rate of 1°C min<sup>-1</sup>, the circumstances appear to be inverted. In the case of the crystallization enthalpy, the values obtained are practically identical, with crystallinity values of around 56%.

It is well known that, as well as depending on the level of dispersion of the nucleating agent, the heterogeneous nucleation of iPP in these systems is controlled by the interactions between the polymer and the nucleating agent, which can be of a chemical or a physical nature, such as epitaxial crystallization,<sup>11,32-36</sup> but the mechanisms by which they act are still relatively unknown. It is important to point out that when the activity of DBS<sup>16</sup> in iPP is compared with that of classical nucleating agents such as salts of aromatic acids,<sup>37-39</sup> DBS not only generates an important increment in the number of nucleation centers, but also higher



**Figure 8** Variation in the relative intensity of the reflections of the (110) and (040) planes of iPP as a function of concentration of MILLAD 3988.



**Table II Dynamic Crystallization Cycle for the STEAMIC 00S/MILLAD 3988 System, Temperatures, and Enthalpies of Crystallization**

% Nucleating Agent	$T_{c10}$ (°C)	$\Delta H_{c10}$ (Jg <sup>-1</sup> )	$T_{c5}$ (C)	$\Delta H_{c5}$ (Jg <sup>-1</sup> )	$T_{c1}$ (°C)	$\Delta H_{c1}$ (Jg <sup>-1</sup> )
0	110.1	93.5	113.2	94.8	121.2	94.9
0,5% MILLAD 3988	129.6	100.2	133.6	100.9	138.7	102.3
1,5% STEAMIC 00S	122.4	98.4	126.5	99.9	134.3	100.2
0,5% MILLAD 3988 and 1,5% STEAMIC 00S	129.1	100.8	133.1	100.5	134.7	98.4

nucleation rates, which evidently reduces to some extent the size of the crystalline superstructures which develop, generating an overall improvement in the mechanical and optical properties. Millner and Titus<sup>40</sup> suggested that the presence of two adjacent hydroxyl groups is critical in the nucleating activity of the sorbitol derivatives and is based on the formation of a nucleating dimer via hydrogen bonds between the diol moieties. They concluded that polypropylene binds to the dimer forming a ternary complex, thus reducing the entropic barrier for crystallization by limiting the local movements of the polymer segments at the points where they are bound to the nucleating agent. Later, it was pointed out from results of molecular modeling that the nucleating capacity of DBS and its derivatives may be related to van der Waals interactions of individual molecules of the nucleating agents with the 3<sub>1</sub> structure of polypropylene, without the previous dimer formation,<sup>36</sup> although from the analysis of the influence of

trinaphthylidene sorbitols on the crystallization of polypropylene, it has been demonstrated that stereoisomerism is an important factor in this type of compound.<sup>41</sup> The DBS molecule is chiral and presents a chevron structure where the aromatic rings assure a good compatibility with the polyolefins at high temperature, and where the hydrophilic part of the molecule is capable of forming self-assembled structures through hydrogen bonds via the free hydroxyl groups. With this structure, during the cooling process, a thermoreversible gel-like phase is formed which is constituted of fibers of DBS interacting with the polyolefin. These DBS gels, whose viscosity is dependent on temperature and concentration,<sup>42</sup> are formed by finely intertwined networks made up of filaments with a thickness of around 10 nm, which produce a continuous string of nucleation centers where polypropylene crystallizes epitaxially.<sup>43</sup>

In Table III, some values of the crystallization temperature of iPP nucleated with sorbitol

**Table III Comparison of the Nucleating Efficiency of iPP with Sorbitol Derivatives**

Nucleating Agent	% Wt	$v$ (°C min <sup>-1</sup> )	$T_c$ (°C)	References
DBS	0.25	10	109.0	44
DBS	0.3	5	122.0	45
DBS	0.4	10	123.2	19
DBS	0.5	10	123.0	41
DBS	2	10	121.6	43
EDBS	2	10	129.9	43
MILLAD 3988	0.025	10	114.7	This work
MILLAD 3988	0.05	10	116.1	This work
MILLAD 3988	0.3	10	128.7	This work
MILLAD 3988	0.5	10	129.6	This work
MILLAD 3988	1	10	129.8	This work
GENISET MDG001	0.1	10	115.4	This work
GENISET MDG001	0.3	10	127.4	This work
GENISET MDG001	0.5	10	128.0	This work

derivatives are compared, along with the crystallization conditions, showing a significant increase of around 5–6°C for the nucleating agents used in the present study compared to DBS at similar concentrations, although lower than that used in the case of EDDBS with a polypropylene of higher tacticity (97%). This seems to confirm the hypothesis of Smith et al.,<sup>36</sup> who established that the stabilization of the 3<sub>1</sub> helix of iPP, provided by the nucleating agent in its dimer state and with its chevron structure via van der Waals interactions, reduces the population of iPP helices, which can return to the amorphous state in the melt-to-crystal transformation during the process of crystallization from the melt.

## CONCLUSION

Although far from the ideal situation of self-nucleation of pure iPP, the nucleation efficiency of these sorbitol-based nucleating agents was shown to be between 35 and 40% more efficient than that of talc or of DBS. In all cases, only the monoclinic form of isotactic polypropylene was observed. No synergic effects were observed for binucleated iPP systems. Some evidence was given for the generation of a preferred orientation in the polymer crystals with increasing nucleating agent concentration.

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

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