

Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

NUCLEATING AGENTS IN POLYPROPYLENE

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Abstract

The effects of nucleating agents such as dibenzylidene sorbitol (DBS) (a derivative of sorbitol), pine crystal 1500, sodium and potassium benzoates in commercial grade isotactic polypropylene iPP are studied using differential scanning calorimetry (DSC). Isothermal crystallization kinetics of polypropylene to the alpha phase have been analyzed using Avrami's model. Results indicate that dibenzylidene sorbitol and pine crystal are very effective in increasing the crystallization temperature of the polymer and number of nuclei formed during crystallization.

Keywords: Avrami equation, crystallization, dibenzylidene sorbitol, DSC, isothermal kinetics, nucleating agents, nucleation, pine crystal, polypropylene

Introduction

Crystallization is a process in which the molten polymer is cooled below its melting temperature such that the crystalline order begins to reestablish. Crystallization occurs essentially in two stages, nucleation and crystal growth. Nucleation is a process in which the loose coiled polymer chains orient themselves into the proper conformation and align into a perfect three-dimensional pattern. The site at which the nucleation starts is called the nucleus. During crystal growth polymer chains orient to the three-dimensional pattern on the nucleus and mostly form a spherical crystal cluster which is called a spherulite. Nucleation in polymers may be homogeneous or heterogeneous. Homogeneous nucleation occurs at high super-cooling in pure polymers. Heterogeneous nucleation occurs at relatively low super-cooling, when a foreign body is present in the melt which reduces the free energy barrier for nucleation. These foreign bodies are called nucleating agents or nucleators. A third kind of nucleation called self-nucleation also occurs in polymer crystallization which is caused due to the presence of partially melted polymer, which acts as a nucleus.

Nucleators raise the crystallization temperature. They also shorten time required for crystallization, thus reducing the cycle time in injection molding processes. Nucleators increase the number of crystallization sites in a polymer thus reducing the

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spherulite size. They cause simultaneous growth and thus evenly sized crystals. Smaller evenly sized crystals improve the physical properties of the polymers like transparency, surface gloss and impact strength.

Several possible candidates for nucleators for polyolefins have been studied for several decades [1–8]. Metal aromatic carboxylates have been employed as nucleating agents for many years. Binsbergen [3] investigated the physical and chemical nature of about 2000 nucleating agents and concluded that most agents are insoluble in the polymer and the soluble agents crystallize out of the polymer melt prior to polymer crystallization. Several different kinds of pigments such as indigosol brown IRRD, indigosol red violet IRH, Cibantine Orange HR etc., have been used as beta-nucleators for polypropylene [9].

A significant breakthrough was achieved with the advent of sorbitol based nucleators. Unlike the conventional nucleators which are of the dispersion type, sorbitol based nucleators are dissolution type nucleators. By dissolution type we mean that the nucleator dissolves in the polymer at the melting temperature of the polymer, whereas dispersion type nucleators are dispersed in the polymer and remain in solid state at the melting temperature of the polymer. DBS (a product of Milliken) was the first sorbitol based nucleator to gain commercial acceptance by the polypropylene industry [10]. However DBS has certain disadvantages such as evaporation during processing and bleeding out from the iPP film. Attempts have been made to overcome these problems by modifying the structure of DBS. This is done by incorporating additional functional groups such as a methyl side group in dimethylbenzylidene sorbitol (MDBS) [10] or meta or para derivatives such as di-*p*-chlorobenzylidene sorbitol [11]. Irrespective of the modifications made in side groups of DBS, the basic structure of these sorbitol-based nucleators remains the same. This purpose of this study is to experimentally examine the nucleation ability of sorbitol based additives along with a rosin based natural product (pine crystals) employing differential scanning calorimetry.

Evaluation of development of crystallinity in polymers can be done in two ways [12]: First, measurable information such as density, crystallinity and thermal energy difference (DSC) and second, direct observation of the spherulite formation using light microscopy. The DSC is a simple and widely accepted technique for understanding crystallization and melting behavior of substances. Results of DSC studies can be used to determine the number of nuclei and mode of crystallization using the Avrami equation [12, 13]. Gaceva [14] used isothermal and non-isothermal DSC to understand the behavior of crystallization and melting of iPP and analyzed the results using Avrami, Ozawa and Harnisch–Muschik methods. Fillon *et al.* [15–17] investigated the self-nucleation and recrystallization of iPP. As our interests are only heterogeneous nucleation we avoided self-nucleation in these experiments by heating above the equilibrium melting temperature and equilibrating at higher temperature for considerable time such that the polymer completely melts before starting the cooling process.

In this work, isothermal and non-isothermal experimental results are presented. The main objective of this study is to reveal the nucleating mechanism of DBS and similar molecules in iPP. Quantitative analysis of these experiments is done based on

Avrami's model. Avrami's model does not cover the entire process of crystallization because it does not account for the secondary crystallization and change in volume during crystallization which are predominant at later stages of crystallization. Rigorous improvements of Avrami's equation in terms of theoretical and experimental techniques have been attempted [18–27]. These improvements include modification of Avrami's equation with addition of more parameters, modifying the equation to tackle non-isothermal crystallization kinetics and using infra-red spectroscopy [28] or rheological mechanism [29] to model isothermal crystallization. It has been observed by Hay *et al.* [30] that secondary crystallization does not play an important role in iPP crystallization. Since the goal of this work is to reveal the mechanism of nucleation which occurs at the early stage of crystallization, Avrami's model is found to be satisfactory.

Experimental

Sample preparation

The degree of dispersion of nucleating agents in iPP is crucial for reliable and repeatable results. Dissolving both the polymer and the nucleator in a common solvent and removing the solvent is an effective way to disperse the nucleator in the polymer. A known mass of polypropylene is mixed with the required amount of the nucleator and is dissolved in *m*-xylenes at 130°C. Once dissolved the solvent is evaporated in a vacuum oven at 180°C until all the solvent is removed and is then dried for 12 h at 120°C in vacuum. This procedure results in a thick film (~0.1 mm) of homogeneous mixture of the additive and iPP.

Approximately 5 mg of the sample is kept in an aluminum pan and used for DSC experiments. Every experiment is immediately preceded by a complete thermal cycle consisting of heating, equilibration and cooling, such that the previous thermal history is erased during heating and equilibration and constant cooling rate establish the common thermal history for all the runs.

Isothermal experiment

Isothermal crystallization is the process by which a polymer is cooled rapidly from its melting temperature to a constant temperature (T_c) below the melting but above the glass transition temperature. The experimental isothermal temperature and time required for complete crystallization are determined by trial and error. The isothermal experiments were done in the range of 132.5 to 115°C in steps of 2.5°C.

Non-isothermal experiments

Non-isothermal experiments done are primarily constant cooling rate experiments. In this experiments a polymer is cooled from its melting temperature to a temperature (T_c) below the melting using constant cooling rate. The cooling rates used in experi-

ments are $5^{\circ}\text{C min}^{-1}$. Non-isothermal experiments are done in order to determine the rise in crystallization temperature of iPP due to the addition of different nucleators and concentration dependence of addition of DBS.

Equilibrium melting temperature determination

In order to determine the equilibrium melting temperature of iPP and iPP mixtures Hoffman–Weeks plots are made. Several constant rate heating is conducted by followed by variable isothermal crystallizations. This plot shows the relationship of melting temperatures to the isothermal crystallization temperatures.

Results and discussion

Multiple melting endotherms are often observed in polypropylene especially at low heating rates. These are caused due to melting-recrystallization-remelting during heating in the DSC. This process is termed as melt reorganization of iPP which may include an increasing order in crystal spherulites, interfibrillar growth and crystal thickening and the appearance of two different crystal structures [14]. At higher heating rates all the endotherms and exotherms merge together into one resultant endotherm. Figure 1 shows the multiple melting endotherm of iPP at $5^{\circ}\text{C min}^{-1}$ heating. Nevertheless it has been observed that the exotherm caused by crystallization during cooling is unaffected by the heating rate, whereas it depends only on the cooling rate. Crystallization will also be affected by the isothermal melting temperature at which iPP is subjected before crystallization. If this temperature is lower than the equilibrium melting temperature it results in self-nucleation. Equilibrium melting temperatures are determined using Hoffman–Weeks plots in Fig. 2. It is found that the difference in equilibrium melting temperatures are insignificant between DBS

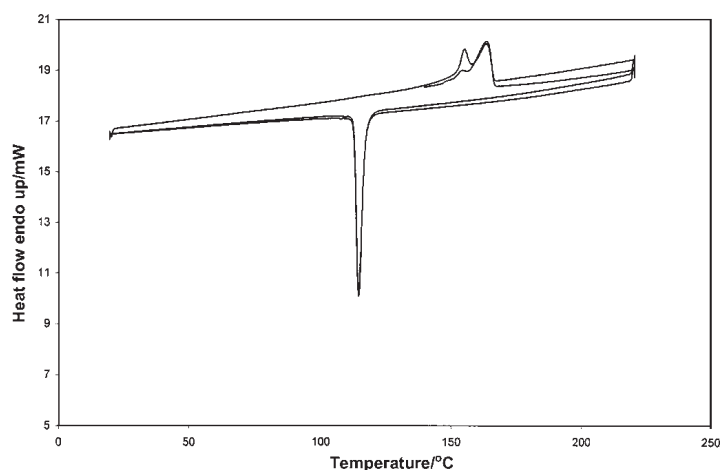


Fig. 1 Multiple endotherms and exotherms during PP crystallization

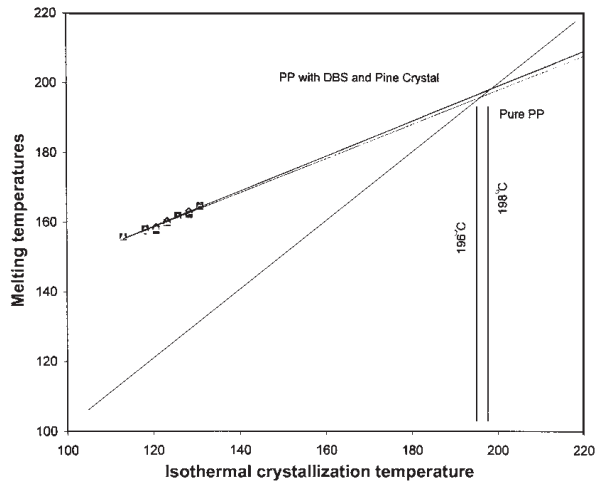


Fig. 2 Hoffman-Weeks plot

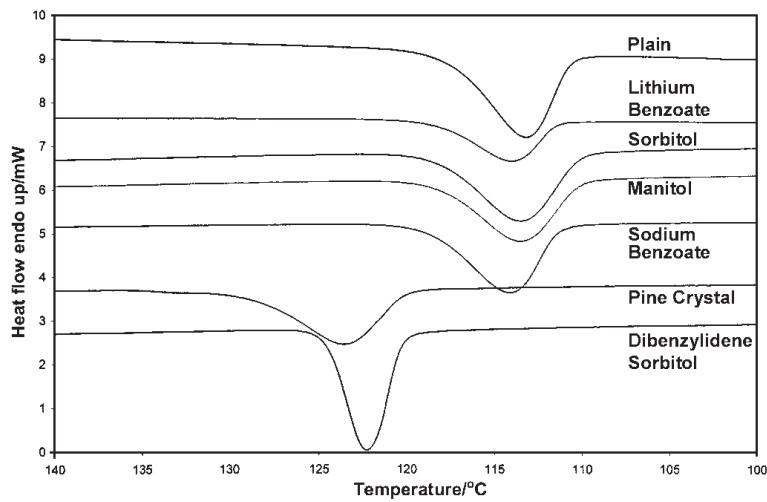


Fig. 3 Effect of different nucleating agents of PP crystallization

and pine crystal nucleated iPP where as a 2°C difference was observed between nucleated and non-nucleated iPP. The values are 196 and 198°C for pure and nucleated iPP respectively. All the following experiments are carried out such that the isothermal melting temperatures are above the equilibrium temperatures so that self-nucleation does not obscure the heterogeneous nucleation conditions which is of prime importance for this work.

In order to compare the effectiveness of the additives, concentrations of all the additives are held constant. The nucleators (or the additives) for experiments are se-

lected from different categories. This study concentrates mainly on DBS, but additives such as sorbitol and manitol were also studied because their chemical structures are similar to DBS. Another type of additive studied are the conventional dispersion type additive for polypropylene such as sodium and lithium benzoate. The influence of different nucleators on the crystallization temperatures are shown in Fig. 3. The cooling curve of iPP with DBS shows a marked sharpness and a high melting temperature. The cooling curve of iPP with pine crystal is rather blunt with a shoulder at high temperature. This shoulder could be attributed to a mechanism similar but opposite to melt reorganization observed during melting which was discussed before. The effect of such a mechanism is more pronounced in pine crystal nucleated iPP probably because pine crystal favours the nucleation of the specific crystal form at high temperature, which eventually dissolves and emerges as the more stable crystal form. This could also be the reason for the blunt shape of crystallization peak observed with pine crystal, as it crystallizes over a longer period of time and wider range of temperatures at constant rate cooling. The crystallization temperature and offset are tabulated in Table 1.

Table 1 Effect of nucleators on melting temperature

Nucleators/0.3%	Peak crystallization temperature/°C	Onset temperature/°C
Dibenzylidene sorbitol	122	124
Pine crystal	123	128
Sodium benzoate	114	118
Lithium benzoate	114	119
Manitol	113	118
Sorbitol	113	118
None	113	117

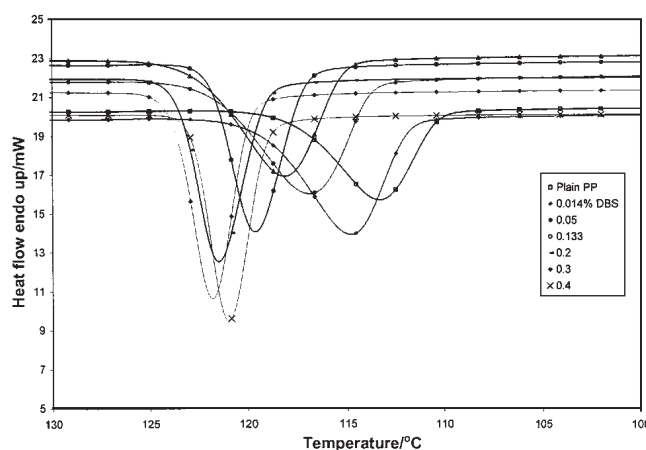


Fig. 4 Concentration dependence on crystallization exotherm

Figure 4 shows the effect of DBS on the iPP crystallization at various concentrations. It can be observed that as the concentration increases there is a linear increase in melting temperature until a concentration of 0.3% by mass after which melting temperature decreases. This kind of linear response indicates the molecular level interaction of DBS in nucleating iPP. Figure 5 shows the dependence of melting temperature on DBS concentration. This results is in agreement with the findings of Kim *et al.* [18].

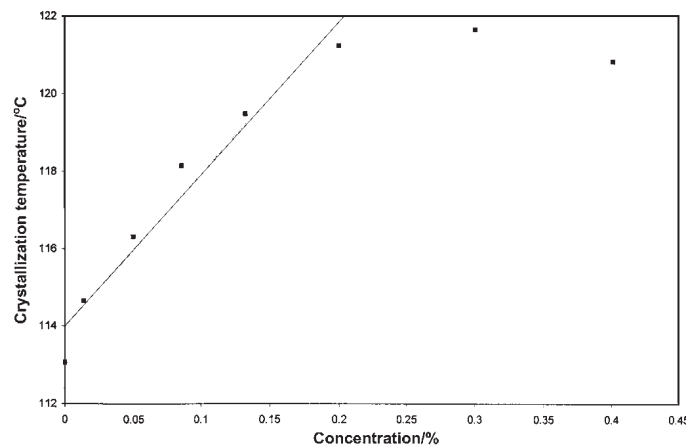


Fig. 5 Concentration dependency of DBS on melting temperature

Isothermal experiments results are shown in Figs 6a and 6b. Note that time is in a logarithmic axis. It can be seen that iPP with DBS nucleates much earlier than that iPP without DBS even at lower super-cooling.

Avrami's analysis

Avrami's equation is shown below.

$$\alpha(t) = 1 - \exp(-Kt^n)$$

where $\alpha(t)$ is the fraction of the total mass that has been transformed by time, t . K and n are Avrami's constant and exponent respectively.

In order to arrive at the Avrami's constant K and exponent n these steps are followed.

- Subtract the base line from the exotherm.
- Integrate the resultant exotherm with respect to time.
- Normalize the integrated curve to yield α .
- Plot $\ln(-\ln(1-\alpha))$ vs. $\ln(\text{time})$, where \ln is the natural logarithmic function.
- Slope of this plot gives the Avrami's exponent and the intercept gives the natural logarithm of Avrami's constant.

Table 2 Avrami's exponents of iPP with different additives

Nucleators	Isothermal crystallization temperatures/										Average
	115.00	117.50	120.00	122.50	125.00	127.50	130.00	132.50			
None	2.62	2.56	2.46	2.42	2.61	2.41					2.51
DBS	3.03	3.06	2.94	2.84	2.91	2.91	3.03	2.73			2.95
Pine crystal			2.95	2.84	2.96	2.91	2.95	2.94			2.91
Manitol	2.50	2.48	2.41	2.50	2.65	2.25	2.41				2.47
Sorbitol	2.54		2.72		2.47	2.57					2.58
Sodium benzoate	2.95		2.90		3.01						2.95

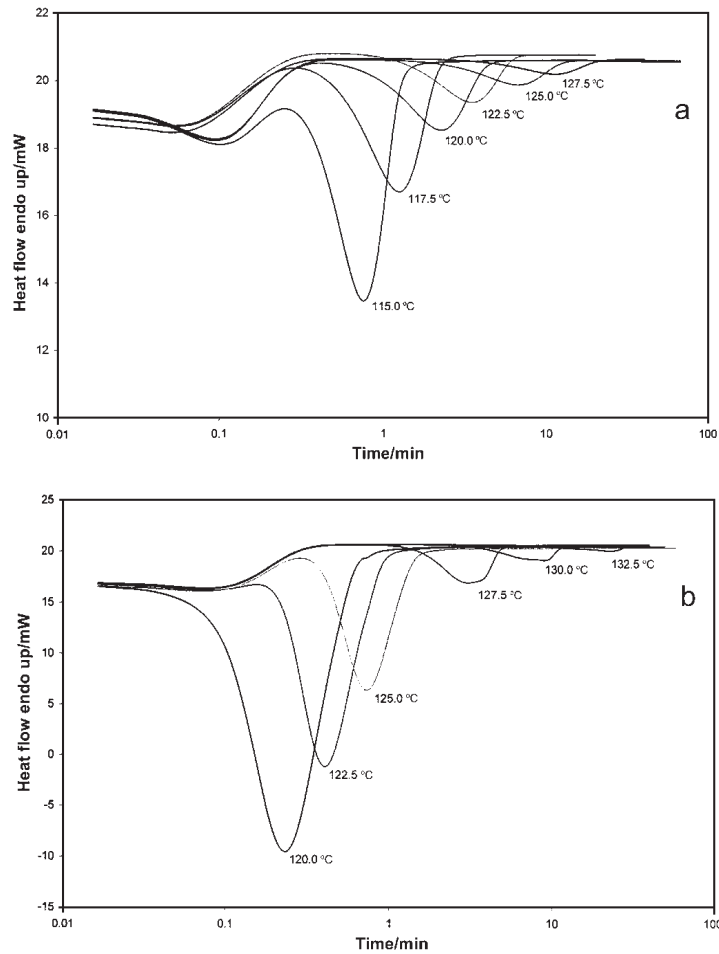


Fig. 6 Crystallization isotherms of PP (a) and PP+0.3% DBS (b)

Avrami's plot for polypropylene with and without nucleators are shown in Fig. 7. It can be observed from these figures that Avrami's equation fits well at low isothermal crystallization temperatures, which are lower than the peak crystallization temperature observed under non-isothermal experiments. The deviation is much more pronounced at higher temperatures, which can be attributed to the shoulder observed at these temperatures. The shoulders are result of a mechanism similar but opposite in nature to the multiple endotherm observed during melting.

Avrami's constant depends on number of nuclei and the spherulitic growth rate. Growth rate is a characteristics of the polymer and depends only on the crystallization temperature. Hence it can be assumed that the growth rate is not influenced by the nucleators. Avrami's constant can therefore be used to compare the nucleating ability

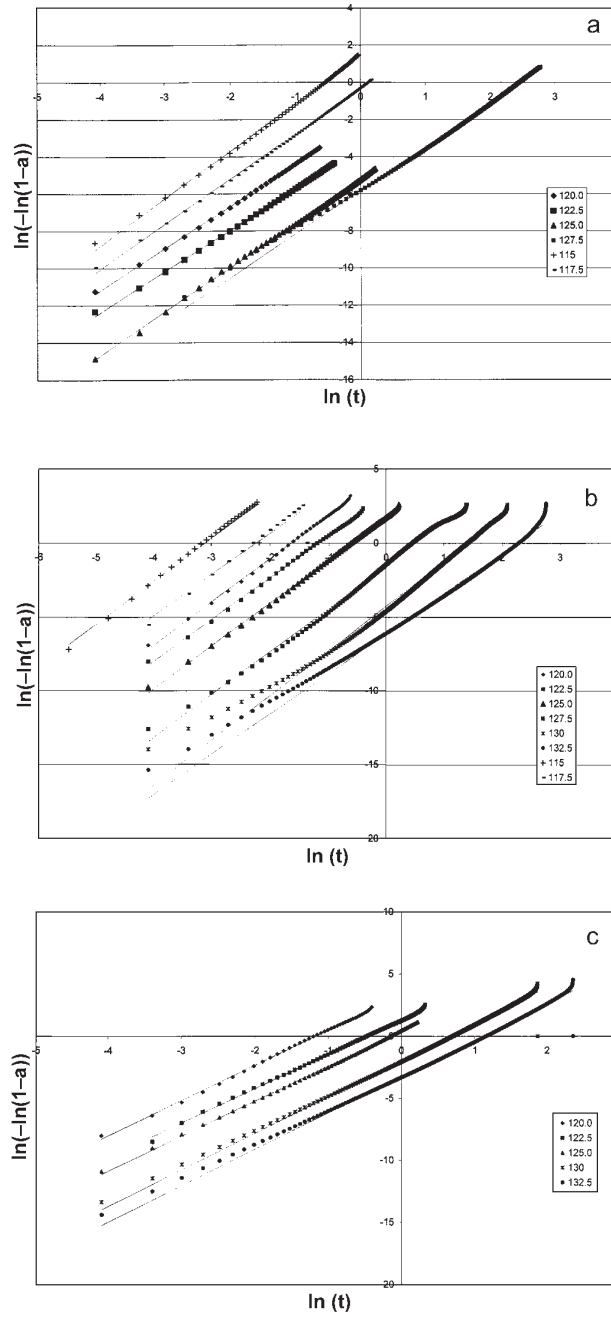


Fig. 7 Avrami's plot of polypropylene (a), with DBS (b) and with pine crystal (c)

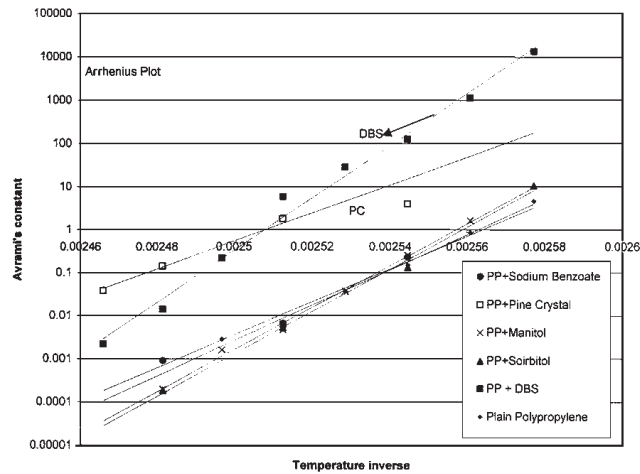


Fig. 8 Arrhenius plot of Avrami's constant

of different additives. Avrami's constant follows the Arrhenius type relationship and is shown in Fig. 8. It can be observed that the number of nucleus formed by DBS and pine crystals at 115 and 132.5°C respectively, are 1000 times more than that formed in pure polypropylene and polypropylene nucleated using conventional nucleators.

Table 2 lists the Avrami's exponent obtained from the calculations. According to Heimenz [31] a value of 2.5 and 3 of Avrami's exponent is expected for sporadic and simultaneous nucleation modes respectively for spherical crystal geometry. As expected pure iPP shows a sporadic nucleation, whereas other additives except sorbitol and manitol shows simultaneously mode of nucleation. In spite of the structural similarity with DBS, sorbitol and manitol do not seem to nucleate iPP. The basic assumption for this conclusion is that the spherulites formed during our experiments are all spherical, which is true for the size of sample we used.

Conclusions

The effects of nucleating agents in polypropylene crystallization are studied using DSC. By investigating Avrami's constants it can be seen that DBS creates 1000 times more nuclei than pure PP at certain conditions suggesting molecular level nucleation. This theory is also supported by the results showing that nucleation by DBS is concentration dependent and that DBS is effective as a nucleator even at concentration as low as 0.014% by mass. The results also show that the crystallization temperature is linearly proportional to the DBS concentration. As the structure of pine crystal is not available in the literature explanation as to the mechanism of action cannot be given.

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