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The Mechanism of Action of Sugar Acetals as Nucleating Agents for Polypropylene

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ABSTRACT: We studied the nucleation of polypropylene via experimental measurements and molecular modeling, and we propose that sugar acetal nucleators stabilize the helical form of polypropylene at the molecular level. Through FTIR techniques, we established that the nucleators dibenzylidene sorbitol (DBS) and trinaphthylidene sorbitol are chemically stable in molten polypropylene. Using solid-state NMR, we determined that DBS is dispersed to particles 32 Å in diameter. These particles are three orders of magnitude smaller than the 1–10-μm size expected in the literature. DSC was employed to evaluate the nucleating ability of our nucleators. Through molecular modeling, we demonstrated that nucleating ability can be correlated with van der Waals attractions of the individual nucleator molecules with the helical form of polypropylene. A correlation was not seen when hydrogen-bonded nucleator dimers were used. The model correctly predicted that one TNS diastereomer nucleates polypropylene and that the other diastereomer does not.

1. Introduction/Background

Our goal is to understand how nucleating agents nucleate polypropylene and to use these results to design a better nucleator for polypropylene.

Polypropylene is a semicrystalline polymer. Isotactic polypropylene is 67% crystalline.[1] As the isotactic fraction decreases to 60%, the crystallinity decreases to 40%. The noncrystalline regions are amorphous. The crystalline regions contain polypropylene in a helical conformation.[2] This helical conformation minimizes the steric clashes of the methyl groups of polypropylene along its backbone.

Nucleation first requires the polymer to be heated above its melting temperature (T_m) and then cooled below its T_m. At the T_m, the polymer chains in the crystalline regions gain motion, and the crystals begin to soften.[3] Above the T_m, the crystals melt and the crystalline regions of the polymer become flexible and amorphous. When the molten polypropylene is cooled, the crystalline order begins to be reestablished. This process is called crystallization.

In the crystallization process there is an opposition of favorable van der Waals interactions with unfavorable entropy.[4] As one continues to cool polypropylene below its T_m, its helices become more stable. At first, the helices revert to random coils as quickly as they are formed. But as the temperature drops further, helices begin to predominate. Cheng and Wunderlich[4] describe the crystallization process in seven steps/reversals: (1) primary nucleation/melting, (2) diffusion to/from the interface, (3) disentanglement/entanglement, (4) absorption/desorption, (5a) surface nucleation/melting, (5b) molecular nucleation/rejection, (6) crystal growth/melting, and (7) crystal perfection/melting.

The site where the nucleation process begins is usually termed the nucleus. From this site, polypropylene helices extend and fold into lamella-shaped structures.[5–7]

The lamellae twist as they grow out from the core and form a complex, spherical crystal or spherulite. The spherulite contains the twisted lamellae as well as the amorphous area between the lamellae. A spherulite continues to grow until it impinges on another spherulite.[8] As the temperature is lowered below the glass transition, the molecular motion becomes too slow to allow a random chain to acquire a crystalline form.

Are spherulites perfectly structured crystals? No. For example, a tie molecule is formed when one end of a polymer chain is incorporated into one lamella or spherulite, and the other end is incorporated into a different lamella or spherulite. This forms a molecular bridge between the lamellae or spherulites. These bridges increase the strength required to separate one spherulite from another. Taut tie molecules substantially increase the small elasticity modulus of the amorphous layer.[8] The addition of a nucleator also produces an increased elasticity modulus.[9] Since nucleators increase the number of crystal growth sites and number of spherulites in a polymer, one would expect a proportionate increase in the number of tie molecules in a nucleated polymer. An increase in tie molecules would explain the increase of elasticity modulus seen in nucleated polymers.

Nucleation increases the number of crystal growth sites in a polymer. There are three routes of nucleation: self-nucleation, homogeneous nucleation, and heterogeneous nucleation.[10] Self-nucleation arises from polymer crystals which did not melt in the melting process. Homogeneous nucleation is the primary process for crystallization during rapid cooling of the molten polymer if no preformed nuclei or foreign surfaces are present. This type of nucleation is present in pure virgin polymer which has been heated well above T_m to melt the polymer completely. In homogeneous nucleation the polymer chains themselves provide the nucleating sites.

The third route, heterogeneous nucleation, arises from a foreign agent which provides nucleating sites. The foreign substance provides a surface which reduces the free energy barrier to primary nucleation.[11] The heterogeneous nucleating agents shorten the induction time for crystallization, because the polymer melt does not have to form its own seeds to initiate crystallization.[12]

Heterogeneous nucleation provides many more sites for nucleation to occur than are available from homogeneous nucleation. This increases the crystallization rate and the

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number of spherulites in a polymer, and it decreases the size of the spherulites. When the spherulites are smaller than the wavelength of light, they do not refract light. This results in clearer polymer.

Nucleators increase the flexural modulus and tensile strength of the final polymer.[13] Heterogeneous nucleation also increases the percent crystallinity for polyamides and polyethylene terephthalate, because a higher proportion of the polymer chains can crystallize before the temperature of the polymer goes below its glass transition temperature. One could argue that since the crystalline phase is much less flexible, this increase in crystallinity is responsible for the measured increases in the flexural modulus and the tensile strength of the final polymer.

Which polymers are affected by nucleation? Polyethylene of MW = 100 000 has a fast maximum crystal growth rate of 83 000 nm/min.[11] This rate is so fast that heterogeneous nucelation does not have a dramatic effect on its crystallization rate. Atactic polystyrene has a very slow crystal growth rate. Its crystallization rate is so slow that it does not crystallize.[9] Polypropylene of MW = 100 000 has a maximum crystal growth rate of 330 nm/min.[11] Nucleation is very effective in increasing polypropylene's crystallization rate and thus improving its properties. Godovskii studied the crystal growth rates of polypropylene and 22 other polymers and found that the maximum crystal growth rate is at $0.82T_m$ to $0.83T_m$ regardless of the polymer or its melting point.[14]

The properties which are improved by nucleation include an increase in clarity, hardness, tensile strength, and elasticity modulus.[9] Since the polymer crystallizes faster, injection molding cycle times are reduced which decreases the cost of the process.[15]

The effects of a nucleator on a polymer's properties are well-known. Unknown is how a nucleator actually works and how to design a better nucleator.[16] In the past the design of nucleators has been by trial and error. New nucleators were discovered empirically, and their characteristics were compared. Jansen listed four characteristics of a nucleator: (1) lack of solubility in the polymer, (2) lower melting point than the polymer, (3) dispersed to a 1–10-μm particle size, and (4) wetted or absorbed by the polymer.[9] Chatterjee, Price, and Newman found that strong nucleators need not be (1) similar in chemical structure to the polymer, (2) similar in crystallographic unit cell type, or (3) a close match of crystal lattice parameters with the polymer.[17] They also found that nucleating ability is not related to the surface energy of the nucleator.

Alkaline-earth metals and salts of organic carboxylic acids, phosphoric acids, and sulfonic acids are nucleators which do not dissolve or melt in the molten polymer. Instead they leave structured crystalline surfaces which force the polymer molecules into a stretched conformation over a long distance, aiding in crystallization.[18]

Mercier showed that nucleation can sometimes be a chemical phenomenon.[19] A nucleator can react with the polymer producing a product. The product is then the true nucleating species. Sodium 2-chlorobenozate, for example, cleaves poly(ethylene terephthalate) via a nucleophilic attack of the carboxylate on the ester group of the poly(ethylene terephthalate). The chain scissions and ionic end groups associate in clusters and form heterogeneous nuclei. The precipitated polymer chains can react with one another to form disodium terephthalate and a rebuilt chain.

Titus and Millner investigated one class of nucleators, aromatic acetals of sugars.[20] There are three nucleators on the market in this class. Milliken sells two: Millad 3905 (dibenzylidenesorbitol) and Millad 3940 [bis(*p*-methylbenzylidene)sorbitol]. Mitsui sells NC-4[bis(*p*-ethyldibenzylidene)sorbitol]. All three commercial agents contain two neighboring free hydroxyl groups (diol). Titus and Millner analyzed nine nucleating agents, including the three commercial materials. They found that dibenzylidene xylitol and bis(*p*-methylbenzylidene) xylitol, which do not contain a diol, performed poorly as nucleators. They then concluded that the diol was "critical for activity". From this assumption, they carried out molecular mechanics and molecular dynamics calculations to understand and design novel nucleating agents.

Titus and Millner's molecular mechanics and molecular dynamics calculations yielded a model in which dibenzylidenesorbitol forms a hydrogen-bonded dimer. This dimer is stabilized by two hydrogen bonds connecting the diol of one nucleator to the diol of the other nucleator. The dimer forms a v-shaped cleft. Polypropylene then binds to this dimer to form a "ternary complex". Titus and Millner claim this binding "reduces the entropic barrier to crystallization by reducing the local motion of the polymer segment at the point of nucleator binding".[20]

Our goal is to design a better nucleator for polypropylene. Our approach is to (1) formulate a working model of nucleation, (2) predict nucleating ability, (3) correlate predictions with experimental results, and (4) identify the important parameters for a nucleator.

Since there are several classes of nucleators and we expect several mechanisms of nucleation, we chose to study nucleators with the highest nucleating ability on the market or in the literature. These nucleators are diacetals of sorbitol.

2. Experimental Section

2.1. Synthesis—Trinaphthylidenesorbitol. 1-Naphthaldehyde (85.00 g) and D-sorbitol (33.05 g) were combined with water (14.5 mL), dimethyl sulfoxide (23 mL), cyclohexane (700 mL), and methane sulfonic acid (2.2 mL) and heated under nitrogen to reflux. Water was removed by distillation. Heating was stopped after water distillation was complete. The product was filtered from the reaction mixture, washed with aqueous sodium carbonate, and purified by a solid/liquid extraction with a tetrahydrofuran/aqueous sodium bicarbonate (1.25:1) solution to yield 1,3;2,4;5,6-trinaphthylidenesorbitol (58.4 g).[21]

2.2. Melt-Mixing Procedure. The nucleators (25 mg) were added to powdered, isotactic polypropylene (5 g) and tumble-mixed on a roll mill. This mixture was fed into the reservoir of an Instron capillary rheometer, equilibrated at 180 °C for 5 min, and extruded into polymer strands of about 3-mm diameter. The strands were chopped and reextruded under the same conditions in order to provide a better dispersion of the additive in the polymer. Polypropylene alone was also treated similarly to obtain a control sample. The loading of the additives was 0.5% unless otherwise noted.

2.3. Differential Scanning Calorimetry. The melt-mixed sample (10 mg) was crimped in an aluminum cup, heated from 0 to 200 °C at a rate of 20 °C/min, held at 200 °C for 5 min, and cooled at a rate of 10 °C/min. The crystallization temperature (T_{cc}, °C) was measured on an automated DuPont 9900 DSC operating in an argon atmosphere.[22]

Selected samples were also analyzed by isothermal DSC. In these experiments, the samples were cooled to 135 °C and isothermally crystallized at 135 °C/4 h following the 200 °C/5 min treatment.

2.4. Optical Microscopy. The samples which were crystallized isothermally in the DSC were cross-sectioned to 5-μm thickness, and the photomicrographs were prepared in transmitted polarized light (Figure 1).

2.5. Solid-State NMR. Nucleator morphology in the polypropylene was investigated via solid-state ^{13}C NMR. In fact the effect used is homonuclear ^{1}H spin diffusion. However, proton

NMR resolution is poor. While ^{13}C NMR resolution is excellent as seen in Figure 4, carbon spin diffusion is quite limited. Consequently we took advantage of the ability to use cross polarization to monitor ^{1}H spin diffusion with the superior resolution of ^{13}C NMR.[23,24,25]

The diffusion equation for short diffusion times is $\langle x^2 \rangle = aDt$, where D is the diffusion constant, t is diffusion time, x is diffusion distance, and the prefactor, a, depends on domain shape,[23,24,26] Thus a plot of intensity versus the square root of diffusion time is initially linear and an extrapolation of this linear portion of the diffusion curve yields a minimum dimension of the domain. At longer diffusion times, the shape of the curve depends on domain shape so one can in theory determine if the isolated domains are planar, lamellar, or spherical.

2.6. Molecular Modeling. All modeling studies were executed using BioDesign's PolyGraf[27] running on either a VAX 785 computer or Silicon Graphics 4D/25 work station. The Dreiding II force field was used for all simulations.

An isotactic polypropylene chain was built using the polymer builder in BioDesign's PolyGraf. The polypropylene chain was 15 monomer units long and fixed in a 3:1 helical conformation. We only used one stereoisomer of polypropylene.

After the nucleator structure was built, we added the polypropylene chain at a distance from the nucleator. The polypropylene structure was fixed, and the nucleator was allowed to move into an energy minimum. Systematic searches were made for minimum energy configurations using the "con min" feature of PolyGraf. This yielded structures in which the polypropylene fit neatly into the groove of the nucleator. A search for a minimum energy conformation yielded a structure in which the polypropylene fit neatly into the groove of the nucleator.

The polypropylene was then separated from the nucleator, the aromatic rings of the nucleator were rotated, and systematic searches were again made for minimum energy conformations. This process again yielded a structure in which the polypropylene fit neatly into the groove. This process was repeated for several orientations of the aromtaic rings on the nucleator until we were satisfied with the minimum energy conformation. Using the above process, each nucleator yielded a structure in which the polypropylene fit into the groove of the nucleator.

2.7. Interaction Energy. For the interaction energy calculations, a number of conformations of the nucleator were explored to find a minimum energy for the isolated nucleator. A polypropylene chain was added to the minimized nucleator, and we explored a number of conformations to find a minimum energy of the nucleator/polypropylene complex.

We defined the binding energy as the energy of the minimized nucleator/polymer complex minus the energy of the minimized *isolated nucleator*. Since the polypropylene was held fixed, its energy remained unchanged in the calculations, was a constant, and was not subtracted for the energy of binding.

$$E_{\text{binding}} = E_{\text{minimized complex}} - E_{\text{minimized, isolated nucleator}}$$

The surface areas were calculated with Polygraph using the standard 0.89 times the van der Waals radius for each atom with corrections for atom overlap. The molecular volume was defined by the surface calculation.

Although the final interaction energies seemed reasonable and internally consistent, we have no way of determining whether global minima have been identified.

Also, we chose only one stereoisomer of polypropylene. Since the sorbitol nucleating agents are chiral, they could have a different interaction energy with each stereoisomer of polypropylene.

3. Results and Discussion

3.1. Formulating a Working Model of Nucleation. We studied nucleation of polypropylene using DSC, Fourier transform infrared (FTIR), solid-state nuclear magnetic resonance, microscopy, and molecular modeling.

3.1.1. Physical State. A nucleated polymer sample crystallizes faster than a nonnucleated sample. The addition of a nucleator to the polymer increases the number of crystallization sites. With more sites initiating crystallization, the crystallization rate of the polymer increases. At a fixed cooling rate (°C/min), the nucleated sample crystallizes at a higher temperature. The temperature of crystallization (T_{cc}) can then be used to evaluate the nucleating ability. The higher the T_{cc}, the better the nucleator.

We evaluated the nucleating ability of the compounds by measuring the T_{cc} of the nucleator/polypropylene blends. For the best nucleators, we evaluated the crystallization rate and spherulite size. Optical microscope pictures were generated from samples crystallized under controlled cooling (Figure 1). With an optical microscope, one shines a light under the sample and records the transmitted light. The individual spherulites are evident under cross-polarized light.

Nonnucleated polypropylene had a spherulite size of 10–15 μm. One can see that these spherulites grew until they impinged upon another (Figure 1a). The thickness of the samples was 5 μm. As a result, the native polypropylene sample contained one layer of spherulites. Spherulite sizes of the nucleated polypropylene samples were much less than 1 μm. The nucleated samples contain several layers of superimposed spherulites in the photograph; therefore, one cannot evaluate the distance between spherulites.

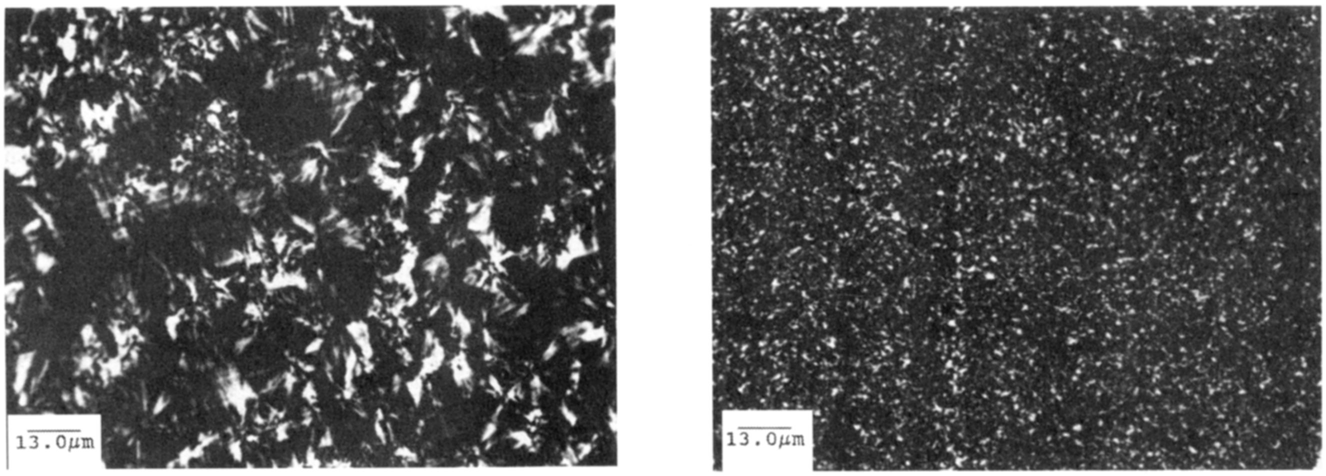
3.1.2. Chemical State. We used FTIR to analyze the chemical state of the nucleators DBS and TNS. We measured FTIR spectra of a virigin polypropylene plaque and of polypropylene plaques which contained 0.25% and 0.50% dibenzylidenesorbitol. Using the spectrum of virigin polypropylene, we obtained the spectrum of the dibenzylidenesorbitol in the polypropylene by digital subtraction (Figure 2). Unlike Mercier's study with poly(ethyl terephthalate), we found that the dibenzylidenesorbitol is intact. There is no decomposition or reaction of the dibenzylidenesorbitol (Figure 3).

A free hydroxyl group has an OH stretch from 3670–3580 cm^{-1}.[28] An intramolecular hydrogen-bonded hydroxyl group has a (usually) sharp OH stretch from 3590–3400 cm^{-1}. An intermolecular hydrogen-bonded hydroxyl group, however, has a broad OH stretch from 3550–3200 cm^{-1}. The dibenzylidenesorbitol in the polypropylene shows evidence for hydrogen bonding. The frequency of absorbance, 3220 cm^{-1}, suggests inter- and not intramolecular hydrogen bonds. Since the nucleator cannot hydrogen bond to polypropylene, it must be hydrogen-bonded to another nucleator molecule. The pure nucleator also absorbs at 3222^{-1} cm, so the dibenzylidenesorbitol in polypropylene has similar hydrogen bonding to neat dibenzylidenesorbitol.

We also studied the FTIR spectrum of trinaphthylidenesorbitol in polypropylene plaques. The trinaphthylidenesorbitol is intact. There is no decomposition or reaction of the trinaphthylidenesorbitol. Since TNS has no free hydroxyl groups, hydrogen bonding is not possible between TNS molecules.

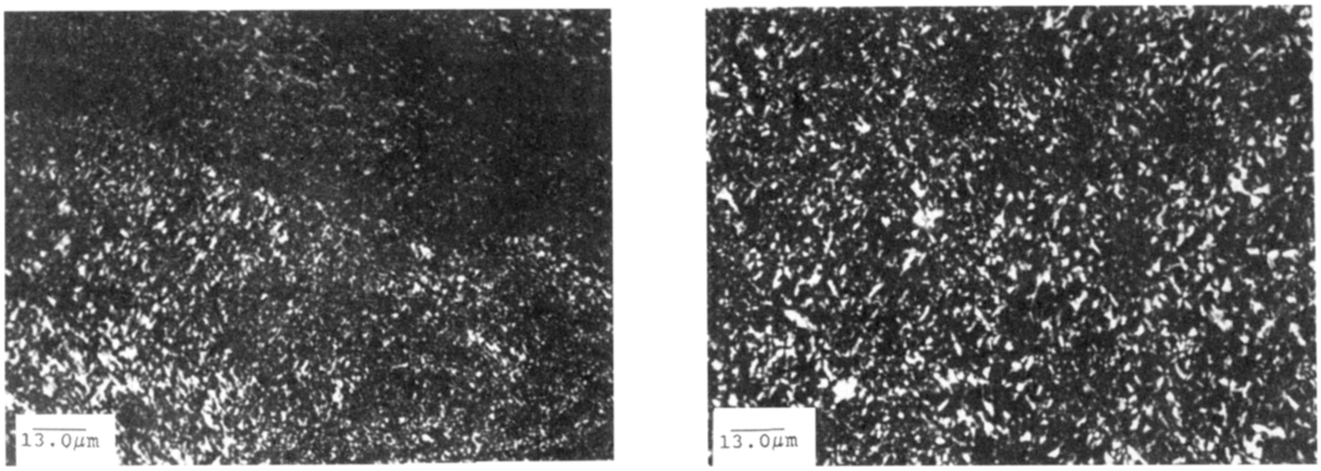
The IR absorbances for dibenzylidenesorbitol and trinaphthylidenesorbitol in the plaques are proportional to the concentration of the added nucleators. Therefore, FTIR may be useful as an analytical technique in determining the final concentration of the additive in a polymer. For the sharp, well-resolved, aromatic bands at 736 and 697 cm^{-1}, we estimate the detection limit at 0.01%.

3.1.3. Domain Sizes. Solid-state ^{13}C NMR was used to characterize the dibenzylidenesorbitol in polypropylene (PP). We determined domain compositions by comparing rates of spin–lattice relaxation in the rotating frame



a) POLYPROPLYENE - CONTROL

b) POLYPROPYLENE + 0.5% MILLAD 3905



c) POLYPROPLYENE + 0.5% MILLAD 3940

d) POLYPROPLYENE + 0.5% TRINAPHTHYLIDENE SORBITOL

Figure 1. Spherulites. Polypropylene was melted and cooled in a press. Photos were taken under a polarized light: (a) control, (b) dibenzylidenesorbitol (0.5%); (c) bis(*p*-methylbenzylidene)sorbitol (0.5%); and (d) trinaphthylidenesorbitol (0.5%).

($T_{1\rho H}^{-1}$). $T_{1\rho H}$ is one of the most sensitive measures known for microphase separation.[24,25] The measurement depends on homonuclear ^1H–^1H dipolar coupling, which is a through space rather than a through bond effect. By the process known as spin diffusion, dipolar coupling will cause all relaxation rates within a given domain to equilibrate very rapidly.[23–26,29–33] If the components of a phase separated material have different relaxation rates, the individual domains will show different relaxation rates. If there is molecular mixing, then one observes an average of the individual relaxation rates. This type of behavior has been observed in a number of polymer blends, semicrystalline polymers, and block copolymers. In this case, we observed different $T_{1\rho H}$'s for the PP and the DBS, consistent with phase separated domains of DBS.

Since spin diffusion is a through space effect, one can also measure domain sizes. While equilibration within domains is quite rapid, equilibration between domains requires that polarization "diffuse" across the interface and redistribute within the domains. The rate at which this equilibrium occurs depends on domain shapes, dimensions, and diffusion constants. A number of spin diffusion methods have been developed in recent years, generally focused on polarization "filters" which will allow one to selectively generate ^1H polarization in one domain and then monitor the growth of signal in the other domain.[23,24,29–33]

In this case, we used a Goldman Shen[33–35] filter to suppress the DBS response, leaving only PP polarization. We then monitored the growth of the DBS signal via spin diffusion with time, as plotted in Figure 5. Clearly, the equilibration time is quite short, indicating very small domains. Using a typical spin diffusion constant for the types of materials (6×10^{-12} cm^2/s) we extrapolated the linear portion of the curve and obtained minimum domain diameters of 32 Å for the phase separated particle. The equilibration time was so short that we were unable to determine whether we are dealing with one-, two-, or three-dimensional spin diffusion. However, it is clear that the DBS particles are quite finely dispersed but are not observed as individual molecules. Molecular modeling indicates that two molecules can be accommodated in 32 Å. If the particle were cubic, it would contain eight molecules.

3.1.4. Predicting Nucleating Ability. We began with the above experimental results and ran molecular modeling studies to formulate a mechanism of nucleation. We chose to model nucleation because crystal growth in polypropylene is a nucleation-controlled phenomenon.[7] Nucleation or nucleus formation is the rate-limiting step.

In the crystallization process there is an opposition of favorable van der Waals interactions with unfavorable entropy.[4] In heterogeneous nucleation a foreign substance provides a surface or nucleus which reduces the free energy barrier to primary nucleation.[11] The free energy barrier represents the entropy required to take a random-coiled polymer and organize it into a crystalline conformation. In polypropylene crystals, polypropylene is in a 3:1 helical

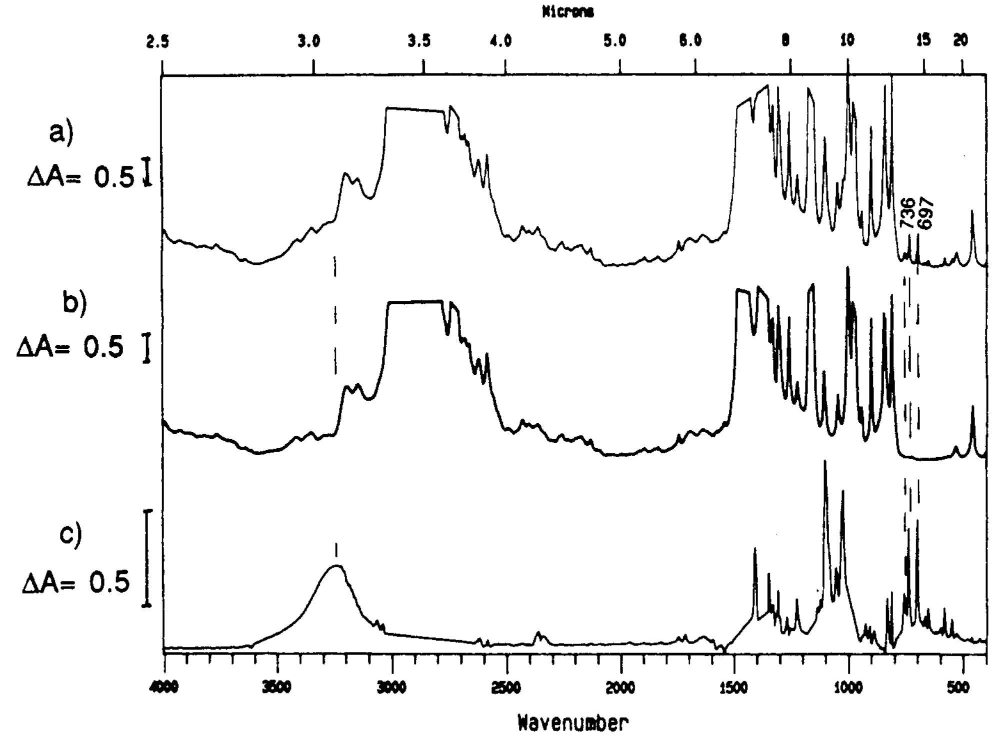


Figure 2. Infrared spectra of (a) a polypropylene plaque containing 0.5% dbs, (b) polypropylene plaque, and (c) digital subtraction spectrum (a–b).

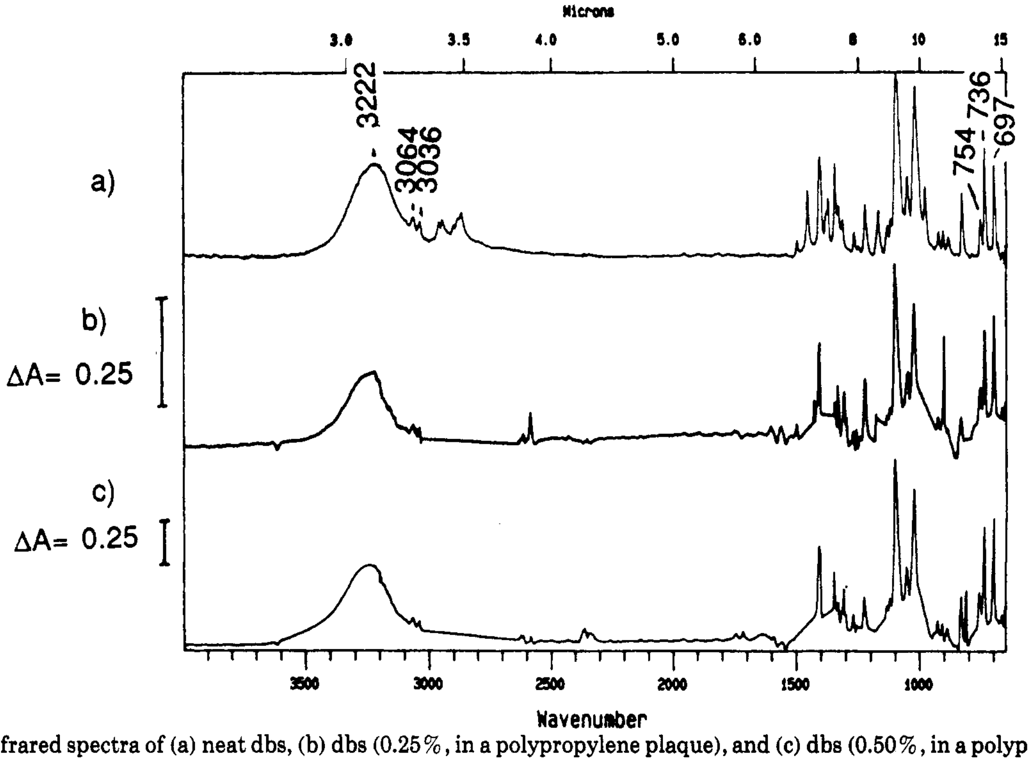


Figure 3. Infrared spectra of (a) neat dbs, (b) dbs (0.25%, in a polypropylene plaque), and (c) dbs (0.50%, in a polypropylene plaque).

conformation.[5] Since helix formation is an entropy-intensive step and nucleators provide a surface which reduces the free energy barrier to primary nucleation, one would expect that a nucleator would be intimately involved with helical formation or stabilization. Titus and Millner evaluated the interaction energy of a nucleator with random-coiled polypropylene.[20] We reasoned, however, that a nucleator has to stabilize the helical form of polypropylene, because polypropylene is in a helical conformation in the crystalline region.

We calculated the interaction energy of various nucleators with helical polypropylene. The interaction energy represents the stabilization energy provided to the helix by the nucleator via van der Waals interactions. Although this does not differentiate between stabilization before or after the helices are formed, we speculate that the nucleators stabilize the helices after they are formed and decrease the numbers of helices that return to a random conformation.

We studied 16 monomer and dimer structures using BioDesign's Polygraf[22] and determined the interaction energy of the mono and the dimer structures. A dimer can be formed when one nucleator molecule forms intermolecular hydrogen bonds to another molecule. We compared our modeling results with our experimental results.

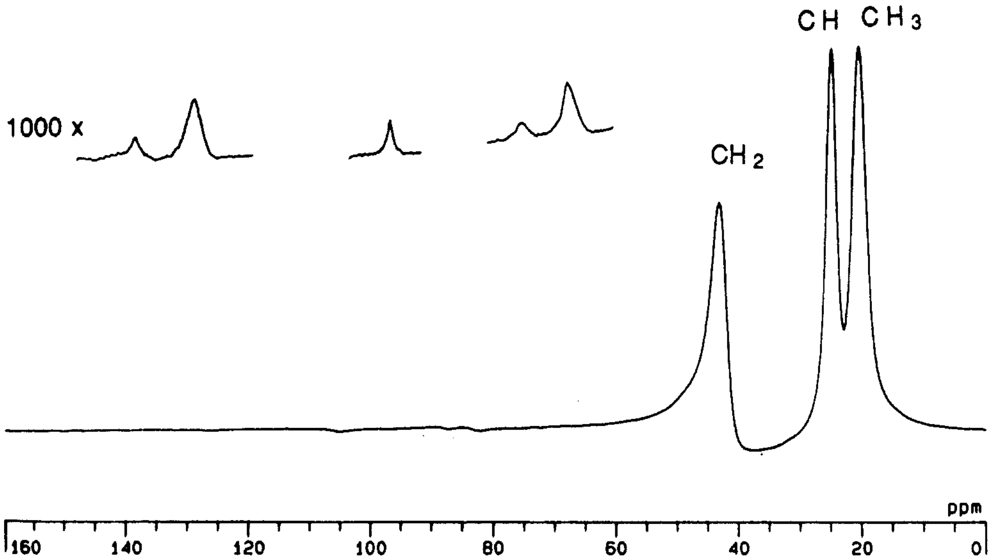


Figure 4. Solid-phase ^{13}C NMR (200 000 scans, ppm) of a polypropylene plaque containing dibenzylidenesorbitol (0.5%).

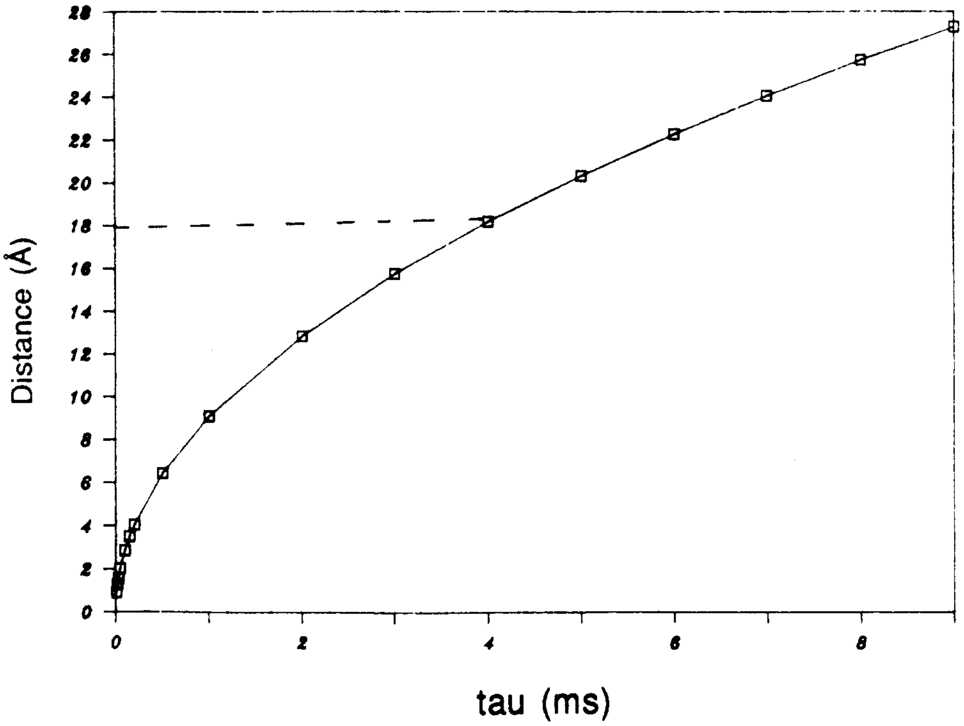


Figure 5. Spin diffusion plot from the solid-phase ^{13}C NMR spectrum.

In the study we fixed the polypropylene in a 3:1 helical structure and allowed the nucleator to minimize in the presence of the polypropylene. Millner and Titus suggested a nucleator "reduces the entropic barrier to crystallization by reducing the local motion of the polymer segment at the point of nucleator binding". We reasoned, however, that the nucleator works by stabilizing the helices. This stabilization binding stabilizes the helices, thereby decreasing the number that return to a random conformation. These helices then grow and form crystals. A good nucleator, then, would have optimum interactions with the 3:1 helix and not with random-coiled polypropylene.

We calculated the interaction energies of the nucleating agents and their dimers with polypropylene as described in the Experimental Section. The binding energy could have been defined as the lowest energy of the minimized complex minus the energy of the polypropylene in the complex minus the energy of the nucleator *in the complex*. However, this type of calculation would ignore the energy it takes for a nucleator to adapt a binding conformation. Some high-energy conformations may have good binding to polypropylene, but based on a Boltzmann distribution, a negligible proportion of the molecules would be in the higher energy, active conformation.

Instead, we defined the binding energy as the energy of the minimized nucleator/polymer complex minus the energy of the minimized *isolated nucleator*. In some cases the lowest energy conformation of the minimized, isolated nucleator was dramatically different from the minimized conformation of the nucleator in the minimized complex. Since the polypropylene was held fixed, its energy remained unchanged in the calculations, was a constant, and was not subtracted for the energy of binding.

$$E_{\text{binding}} = E_{\text{minimized complex}} - E_{\text{minimized, isolated nucleator}}$$

We also calculated monomer and dimer volumes and surface areas. We analyzed the conformations of the nucleator/polypropylene complex and found that all of

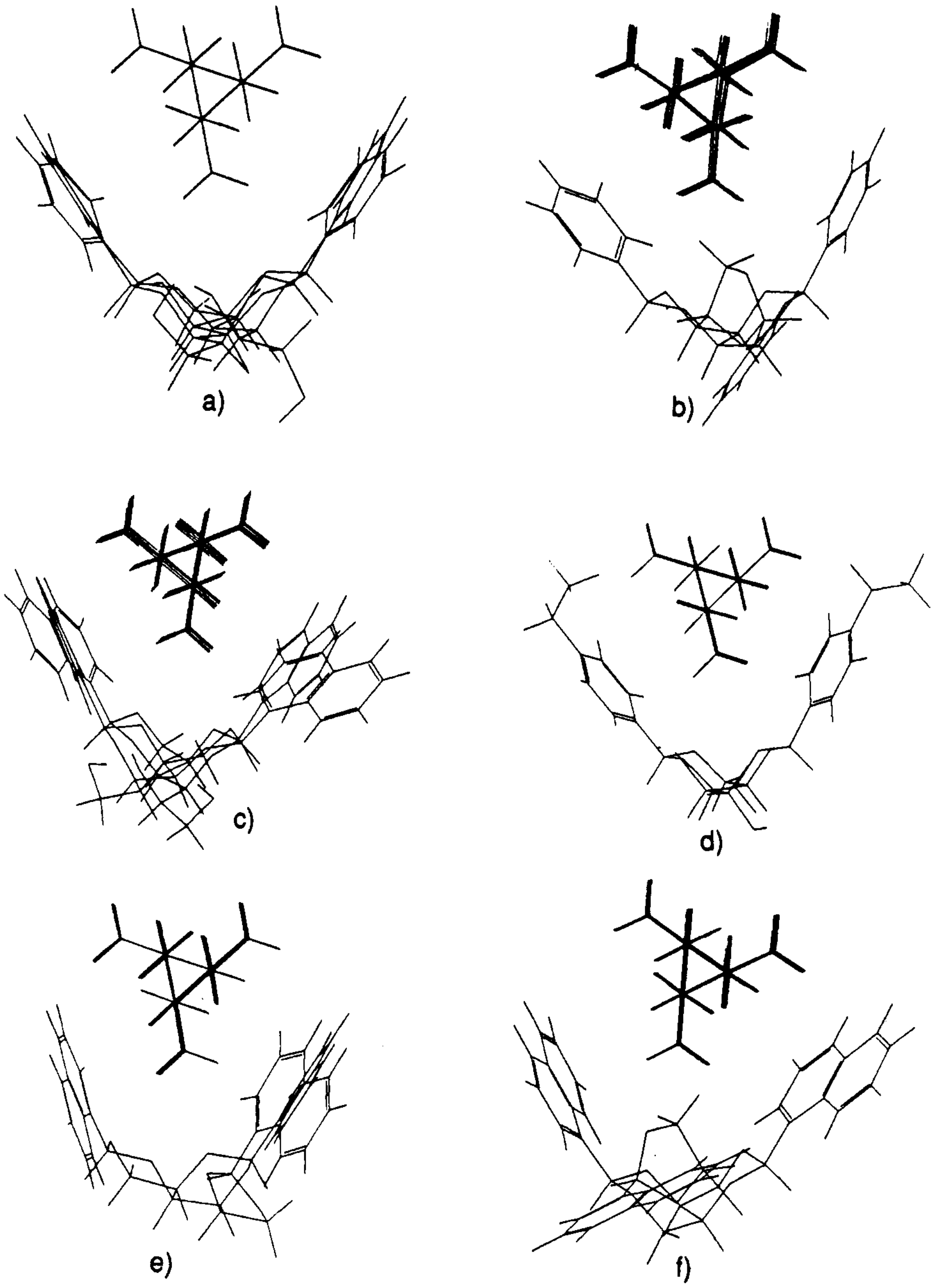


Figure 6. Interactions with polypropylene. Viewed perpendicular to the pp axis: (a) dbs dimer, (b) tribenzylidenesorbitol, (c) dinaphthylidenesorbitol dimer, (d) bis(*p*-ethylbenzylidene)sorbitol, (e) R-tns, and (f) S-tns.

the nucleating agents form a v-shaped conformation.

Dibenzylidenesorbitol (DBS) easily adapts a v-shaped conformation. The polypropylene helix fits snugly into the v-shaped cavity.

Dibenzylidenesorbitol as well as several other nucleators can form a hydrogen-bonded dimer. The interaction energy for the hydrogen-bonded dimer is almost twice the monomer. The cavity for the dimer is 15 Å long and encompasses 2.5 helix turns (Figure 6a).

Tribenzylidenesorbitol has no free hydroxyl groups and cannot form a hydrogen-bonded dimer. Its third benzene ring partially blocks access to the v-shaped cavity and may be the cause of a lower interaction energy than the monomer of DBS (Figure 6b).

Dinaphthylidenesorbitol (DNS) shows a favorable interaction with polypropylene, but the most stable interaction of DNS with polypropylene has DNS in a high energy conformation. A host/guest relationship between DNS and polypropylene is weakened by the amount of energy required to get DNS into the correct conformation (Figure 6c).

Bis(*p*-methylbenzylidene)sorbitol is predicted to be a better binder than dibenzylidenesorbitol. This is presumably due to increased van der Waals interactions of the methyl group which extends the walls of the cleft. For the same reason, ethyl, isopropyl, and *tert*-butyl groups give increasing interaction energies in the monomer form (Figure 6d).

Trinaphthylidenesorbitol (TNS) has two diastereomers. The two diastereomers differ at the acetal between the fifth and sixth carbons of the sugar. One diastereomer has an *R* configuration and the other an *S* configuration at the acetal carbon (Figure 7). Tentative assignment of the isolated TNS diastereomers was made by comparison of the ^{13}C NMR spectra of the diastereomers with the predicted ring shifts for a 2,4-disubstituted-1,3-dioxolane. The modeling studies predict that one diastereomer of TNS should be a better nucleator than the other diastereomer (Figure 6e,f). This was shown to be true experimentally. Whereas the isolated *R*-diastereomer of TNS is a very good nucleator, the *S*-diastereomer is a poor nucleator.[36]

Table 1. Binding Energies of the Nucleators[a]

reagent	energy	energy with PP	binding energy	S.A.	S.A. (dimer)	vol	vol (dimer)	energy vol	energy S.A.	Tcc
dibenzylidenexylitol	66.71	53.29	14.57	382	818	372	741	0.041	0.038	118
dibenzylidenesorbitol	65.90	54.01	13.12	410	500	460	460	0.031	0.028	124
bis(*p*-methylbenzylidene)sorbitol	69.34	55.20	13.20	460	630	604	604	0.026	0.025	128
bis(*p*-ethylbenzylidene)sorbitol	72.75	57.12	15.00	501	969	470	929	0.040	0.037	129
triptycene	80.41	71.44	8.93	298		272		0.033	0.030	111
tribenzylidenesorbitol	84.13	71.55	12.25	500	501	461	461	0.027	0.025	116
dinaphthylidenesorbitol	115.53	98.48	7.83	510	915	414	827	0.043	0.038	111
S-trinaphthylidenesorbitol	134.48	117.70	11.27	630	767	342	685	0.046	0.041	124
R-trinaphthylidenesorbitol	129.83	113.37	20.33							

[a] Energy, −kcal/mol; S.A. = surface area, Å²; vol = volume, Å³.

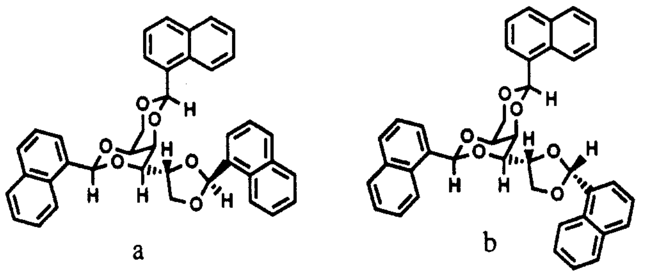


Figure 7. (a) *S*-Trinaphthylidenesorbitol (at the acetal between C5 and C6) and (b) *R*-trinaphthylidenesorbitol.

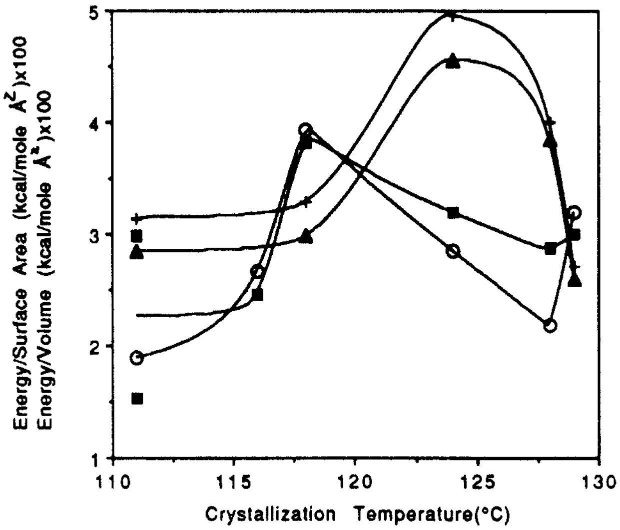


Figure 8. Interaction energies normalized for surface area or volumes of the monomer or dimer structure as a function of crystallization temperature. No apparent correlation. (■) energy/surface area monomer, (▲) energy/surface area dimer, (○) energy/volume monomer, and (+) energy/volume dimer.

Since the above modeling studies suggested that favorable interactions of the polypropylene helix with an aromatic cleft is important, we also studied several other structures which have benzene rings in fixed configurations. Triptycene has benzene rings at 120° angles. This does not match the 60° angles of the 3:1 helix, and so the calculated interaction energy is small. When two triptycenes are held together by hydrogen-bonded carboxylic acids, the interaction energy is almost twice that of a single triptycene. This was observed for all of the hydrogen-bonded dimer systems.

It is interesting to note that there are four helical arrangements of polypropylene. Two are right-handed with opposite inclinations of the methyl side chain, and two are left handed.[2] We chose only one stereoisomer of polypropylene. Since the sorbitol nucleating agents are chiral, they could have a different interaction energy with each stereoisomer of polypropylene.

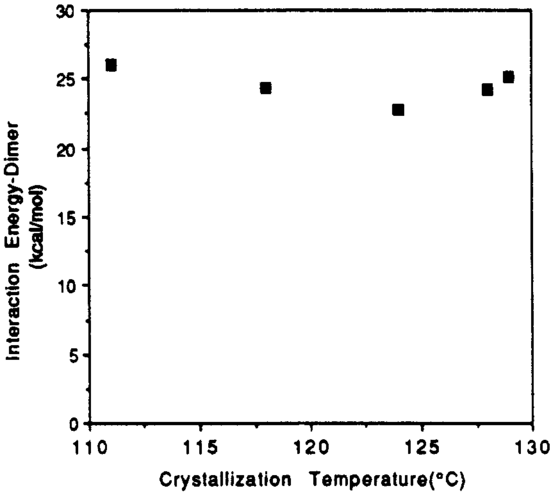


Figure 9. Interaction energy of the dimer conformation as a function of crystallization temperature. No apparent correlation.

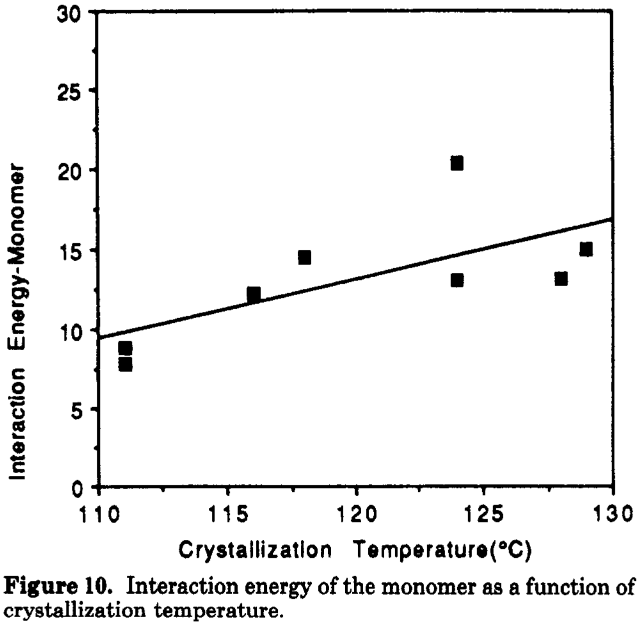


Figure 10. Interaction energy of the monomer as a function of crystallization temperature.

3.2. Correlation of Predictions with Experimental Results. Identification of the Important Parameters for a Nucleator. We compared the measured nucleating ability[21] (Tcc) to the predicted nucleating ability for our nucleating agents and commercially available agents. Our experimental results did not correlate with interaction energy/volume or interaction energy/surface area (Figure 8). Our results also correlated poorly with the interaction energy of the dimer (Figure 9).

Nucleating ability correlated best with the interaction energy of the nucleating agent in its monomer form (Figure 10). The correlation coefficient of monomer interaction energy versus nucleating ability was 0.685. One compound included in this plot was poorly dispersed in the polypropylene sample. This poor dispersion could be visualized by white specks in the polymer. Therefore the effective concentration of this sample was much less than the other samples. This compound represents the data point which is furthest from the predicted value on the graph. When this data point is eliminated from the graph, the correlation coefficient for interaction energy versus nucleating ability is 0.806.

The correlation of monomer interaction energies was surprising, because we began with Titus and Millner's assumption that the dimer was critical for nucleating ability. Our results, however, show that the diol is not "critical" for nucleation. First, monomer energies correlate better than the dimer energies. Second, trinaphthylidenesorbitol, which does not have a diol and thus cannot form a dimer, is a good nucleator (Figure 1).

4. Conclusions

We evaluated the nucleators dibenzylidenesorbitol and trinaphthylidenesorbitol is extruded polypropylene plaques. Through FTIR we found that the particles are chemically unchanged in the polymer matrix. Dibenzylidenesorbitol and trinaphthylidenesorbitol do not react or decompose in the polypropylene. The dibenzylidenesorbitol dispersed in polypropylene has similar hydrogen-bonding to neat dibenzylidenesorbitol. Through solid-phase NMR we found that the nucleator was dispersed to particles which are 32 Å in diameter. This represents particles which are two molecules wide. These particles are three orders of magnitude smaller than the 1–10-μm size expected in the literature.[9] These small particles are very efficient in nucleating polypropylene. In order for these particles to nucleate polypropylene, they must interact with polypropylene in some fashion. Our next goal was to understand the mechanism of nucleation on a molecular level.

We began with the above experimental results and ran molecular modeling studies to formulate a mechanism of nucleation. We chose to study nucleation because crystal growth in polypropylene is a nucleation-controlled phenomenon.[7] In the nucleation and crystallization process there is an opposition of favorable van der Waals interactions with unfavorable entropy.[4] In heterogeneous nucleation, the nucleator added provides a surface or nucleus which reduces the free energy barrier to primary nucleation.[11] We calculated the interaction energy of various nucleators with helical polypropylene. The interaction energy represents the stabilization energy provided to the helix by the nucleator via van der Waals interactions.

Our data supports a nucleation theory in which as the polypropylene is cooled below its melting point, the nucleating agent, in the shape of a cleft, then binds and stabilizes helical polypropylene. This binding stabilizes the helices, thereby either increasing the number of helices or decreasing the number that return to a random conformation. We speculate that the binding decreases the number of helices that return to a random conformation.

We reason a good nucleator has optimum interactions with the 3:1 helix and not with random-coiled polypropylene. A *cis*-diol or a hydrogen bonded dimer is not critical for activity.

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