CHAPTER II

LITERATURE REVIEWS

Since polymer products affect everyday life, much attention has been directed property enhancement with lower cost and manufacturing cycles. Blending additives with polymers is a well-established method to improve their performance. Among the many additives in use with semi-crystalline polymers are nucleating agents. They enhance the crystallization rate and thus shorten the cycle time in some plastics manufacturing processes, and clarifiers. Due to nucleating agents can reduce the crystallite size and hence increase the optical clarity [25]. Nucleating agent have been known since the middle of the last century [26, 27]. Two fundamentally different procedures have been devised to enhance the nucleation density (number of nuclei per unit volume) [28]. The first procedure, self-seeding [29] takes advantage of the intrinsic polydispersity of polymer (large domain of melting temperatures). The polymer crystals are nearly but not completely molten. The crystal residues are used as seeds (nuclei) in a subsequent cooling. The second procedure induced heterogenous nucleation by adding a controlled quantity (less than 1%) of a foreign substance suitable as a crystallization substrate. Both nucleating procedures result in a reduction of the spherulite size. Mechanical and optical properties of thermoplastics strongly depend on the spherulite size [30]. Small spherulites improve flexural modulus, rigidity, heat distortion temperatures while at the same time, impact properties benefit also from the size reduction, haze is reduced and clarity improved.

Conventional nucleating agents

Thierry and co-workers [28] have reported that, the conventional nucleating agents belong to four main groups: salt of aromatic or aliphatic acids, aromatic pigments, hydrazones from aromatic aldehydes, and phylosilicates. These compounds have hardly anything in common: they have different chemical nature and they crystallize in many very different crystallographic systems. Polyethylene (PE) and isotactic polypropylene in its alpha phase (αiPP), the two major crystalline polyolefins

of thermoplastics were used as a polymer matrix. PE and αiPP crystals are different chain conformations and unit cell such as PE: planar zig-zag, orthorhombic unit cell, and αiPP: 3_1 helix, monoclinic unit cell. Most of the nucleating agents, in particular, the salts of aromatic acids have similar organization a sandwich structure with a regular alternation of polar layers and aromatic a polar layer. These planes are lined up by rows of benzene rings bearing or not various substituents. The distance between the furrows depends on the nature and position of the substituents by the benzene rings. In fact, during crystallization, PE chains or prominent methyl rows of iPP can lie down in the furrows defined by the rows of benzene rings. For epitaxial growth of PE on substrates, it was established that the inter-chains distance determines the PE contact plane interacting with substrates [31].

Thus, nucleating agents act via a physical nucleation process, an epitaxial mechanism, a mechanism that is governed by geometrical matching between the polymer and the nucleating agents in the contact planes [32]. Since the past decade, the reduction of crystallization half time in isothermal crystallization and the increase of crystallization temperature (T_C) for non-isothermal crystallization were the criteria to evaluate the nucleating agents. These methods compare the T_C of a nucleated polymer to T_{C0} of the non-nucleated polymer. The T_{Cmax} is crystallization of an ideal seeded sample. Seed produced by self-seeding (the polymer residues from the most stable lamellae) are finely dispersed in the molten polymer, and of cause are fully compatible on both geometrical and chemical groups. Therefore, efficiency scale method have been designed to compared the polymer nucleated by a given nucleating agent at concentration C to both ends of the full nucleation domain, the blank polymer and the ideally self-seeded one [33]. The efficiency coefficient is defined as:

$$E = 100((T_C - T_{C0})/(T_{C\max} - T_{C0}))$$

This simple, convenient and reliable efficiency scale defines a semi-quantitative scale (T_{Cmax} - T_{C0} must be determined for each sample), has significant advantages and helps classify the nucleating agent with a reliable method. The crystallization temperatures are measured with a differential scanning calorimeter

(DSC) [33]. In polymer processing, it was found that addition of small amount of DBS (0.4 % wt) increase of iPP T_C to 10 °C compared to blank iPP with an efficiency of 41%.

In recent reported the discovery of a low-molecular-mass compound which self-assembles into highly extended nanoparticles can be exploited in a similar manner to yield highly anisotropic crystal texture [12]. Essentially, a flow field is used to generate a high level of preferred orientation of the extended nanoparticles dispersed in the polymer melt. On cooling, the aligned nanoparticles direct the subsequent crystallization to yield a material with a high level of lamellar alignment. This striking behavior can be induced in systems that do not normally exhibit a preferred crystal orientation after cooling from a sheared melt without this additive. This behavior has been observed in isotactic polypropylene (iPP) on mechanism by which the crystallization is directed.

Therefore, in this work the sorbitol derivatives were chosen as additive for iPP to investigate the mechanism of the role structure under shear flow and their effect on mechanical properties and morphology polypropylene fiber.

Polypropylene

Polypropylene (PP) is a semi-crystalline polymer that is different in stereospecificity and comonomer content. It can be made from the monomer propylene by Ziegler-Natta polymerization and metallcene catalysis polymerization. The three typical stereo-configuration in polypropylene are: isotactic, syndiotactic and atactic. The tacticity of polypropylene are shown in Figure 3.

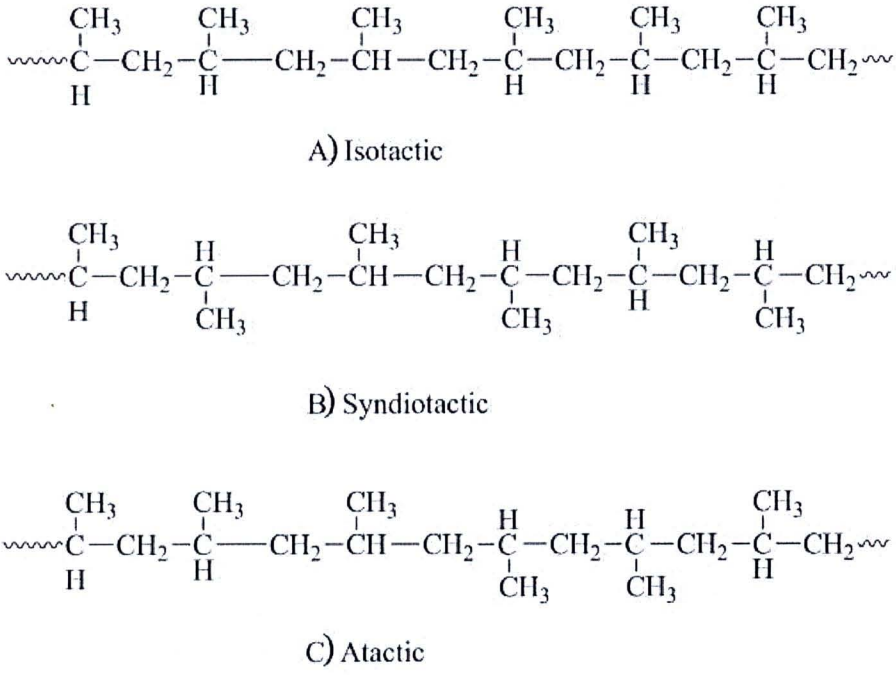


Figure 3 Schematic illustration of the stereochemical configuration of PP A) isotactic PP, B) syndiotactic PP, and C) atactic PP

Isotactic polypropylene (iPP) is a widely used, versatile commodity polymer because of its attractive combination of good processability, mechanical and thermal properties and chemical resistance. iPP is bulkier chains and more complex crystal unit cell arrangement. Thus, nucleating agents can offer a great advantage in industrial processing time. The types of crystal form in iPP including monoclinic (α), hexagonal (β), and triclinic (γ). Besides these crystal structures, a quenched crystal form, called smetatic form was also found [34]. The formation of these crystal forms is dependent upon crystallization conditions and molecular characteristics.

α-form of iPP

The α-crystal modification can predominantly form conventional iPP grade under generally melt and solution crystallization condition. The α-crystal packs in monoclinic unit cell structure (a = 6.66 Å, b = 20.78 Å, c = 6.49 Å) [35]. The crystal structure of α-crystal form shows a helical conformation of the iPP chain aligned on a monoclinic lattice [36-38]. The helical conformation in crystalline state can be formed

by either left- or right-handed helices and possible both into same crystal structure. Some α nucleating agents, such as sorbitol base compound [11,39,40], are also used in iPP.

β-form of iPP [34]

The β-form is generally formed in mixture with the α-form by quenching the melt or by crystallization in the presence of shearing forces. It is normally observed in the presence of nucleating agents. The crystal structure of β-form is hexagonal and packing of helical molecules in the unit cell involves the incorporation of all left-handed or right-handed helices

γ-form of iPP [34]

The γ-form can be generated by crystallization at atmospheric pressure of low molecular weight iPP or by crystallization at elevated pressure of the commercial iPP homopolymer. The unit cell of γ-form is triclinic.

The different forms of iPP crystals are identified by X-ray diffraction pattern as shown in Figure 4.

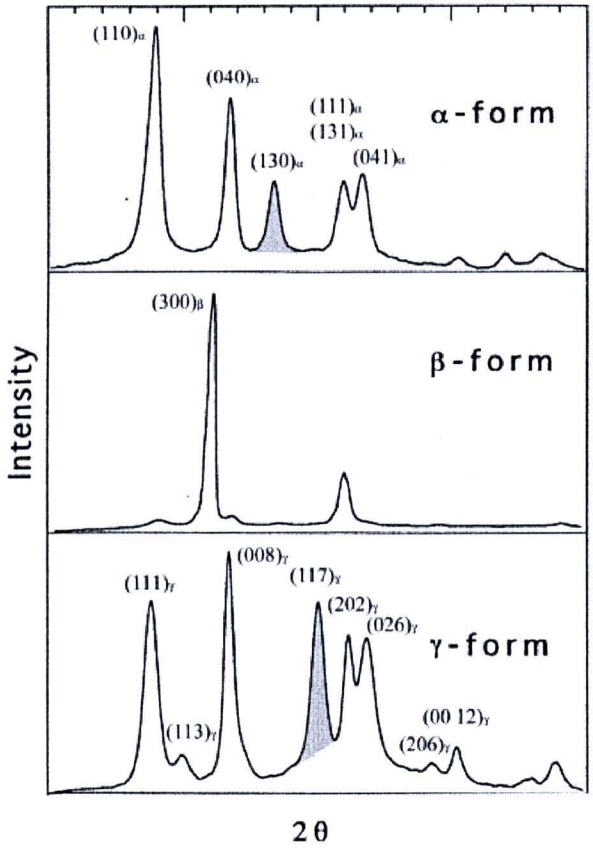


Figure 4 X-ray diffraction patterns of different iPP crystal forms [34]

The mechanical properties and morphology can be controlled by several methods including thermal history, mixing condition, compatibilization of the blends, shear fields, orientation process and nucleation.

The addition of nucleating agents is one of the most important methods to modify morphology and mechanical properties of polymer. It is widely used in the plastic industry.

Dibenzylidene sorbitol (DBS)

Fibril formation of DBS

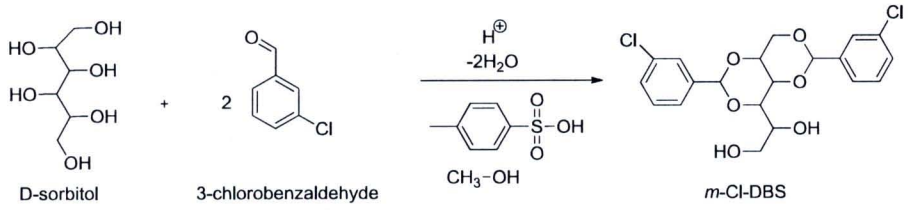
Dibenzylidene sorbitol or 1,3:2,4-dibenzylidene sorbitol (DBS) is a derivative of the natural sugar alcohol D-glucitol [41]. It can be synthesized by a condensation reaction between aromatic benzaldehyde and D-sorbitol [42].

In its native state, DBS exists as a crystalline solid with a melting point of about 220 – 225 °C [43, 44]. The amphiphilic DBS molecule is often described as "butterfly-like" with a sorbitol body and two benzylidene wings. The hydrophobic phenyl rings facilitate DBS dissolution in a wide variety of organic solvents [17]. In addition, in combination with its acetal oxygens and pendant hydroxyl groups, this endows DBS with unique ability to self-organize into nanofibrils and ultimately induce gelation. The discovery of DBS started in the late 1800s by Meunier [45].

Murai and co-workers [46] studied the synthesis of DBS by reacting of sorbitol with benzaldehyde in the presence of a dehydrating catalyst. In this method, cyclohexane was added into the reaction mixture in an amount 5-20 w/w of benzaldehyde. The azeotropic mixture of cyclohexane and water were heated until boil. The azeotropic mixture were condensed and separated to remove the water and recycle the cyclohexane to the reaction.

Uchiyama [47] discovered the purification of dibenzylidene sorbitol by mixing 1 part by weight of crude DBS with 5 to 15 parts by weight of aliphatic alcohol (i.e. methanol, ethanol or iso-propanol). The mixtures were heated at a temperature about 60-70 °C, but below the boiling point of aliphatic alcohol. As a result the monobenzylidene sorbitol and tribenzylidene sorbitol are removed from dibenzylidene sorbitol (DBS). This method gives a purity of DBS at least 98% from crude DBS with a purity of 95%.

Gardlik and co-workers [48] studied the preparation of dibenzylidene-D-sorbitol by dehydration/condensation process, which is shown below.



Furthermore, the polar solvent must be solubilized both of sorbitol and aldehyde. In this purification process, crude DBS was dissolved in aliphatic alcohol (i.e. methanol) for removed mono- and tribenzylidene-D-sorbitol. Due to mono- and tribenzylidene-D-sorbitol can dissolve in methanol. Therefore, the product was dibenzylidene-D-sorbitol.

DBS is known as a gelator which is applied to cosmetics and deodorant gel sticks. It can self-organize to form a 3-D network stabilized by hydrogen bonds at relatively low concentrations in a variety of nonpolar organic solvents and polymers, to produce organogels. DBS constitutes an excellent example of a low-molecular-weight organic molecule that can self-organize into nanoscale fibrils typically measuring from 10 nm to 0.8 μm in diameter through a combination of hydrogen-bonding and phenyl interactions. At sufficiently high DBS concentrations, the nanoscale fibrils form a percolated network that consequently promotes gelation of various organic solvents and polymers. Organogels produced in this fashion have attracted commercial interest due to their many possible applications in cosmetics, personal care products, biomedical materials, and (opto) electronic devices [49].

Anderson and co-workers [50] have invented plastic additives useful as nucleating agent. It can improve the optical properties of polymeric materials. This invention relates to addition of the halogen atom or alkyl group into molecule of benzylidene aditol acetals. They are useful as materials for food or cosmetic containers and packaging. Furthermore, the R_1-R_4 positions in molecule of bis-halogen-alkylbenzylidene alditol acetals which substituted by alkyl group and halogen atom, p

is 0 or 1 the chemical structure as seen in Figure 5 by R_1 and R_3 positions are alkyl groups while The R_2 and R_4 positions are halogen atoms.

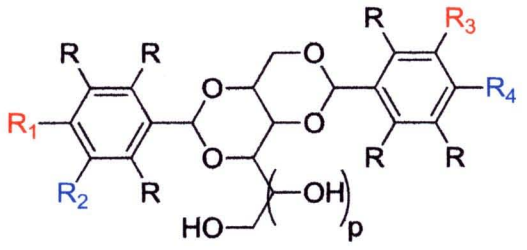


Figure 5 Chemical structure of asymmetric alditol diacetal

This material was mixed with polyolefin such as polypropylene random copolymer and LLDPE. It was found that bis-halogen-alkylbenzylidene alditol acetals can improve the optical properties and increase the crystallization when compared with pure polymer. It can form a gel in various organic solvents and useful as gelling agent, particularly used in preparation of antiperspirant gel sticks.

The chemical structure of DBS is displayed in Figure 6. It reveals that the molecule possesses several sites ideally suited for specific chemical interactions: (i) one pendant hydroxyl group, (ii) one terminal hydroxyl group, and (iii) four acetal oxygen moieties [51]. Infrared spectroscopy [52], as well as molecular modeling calculation [53, 18], of DBS molecules in organic solvents indicates that the pendant hydroxyl group tends to hydrogen-bond intramolecularly to its nearest-neighbor acetal oxygen, whereas the terminal hydroxyl group readily establishes intermolecular hydrogen bonds with the acetal oxygens on adjacent molecules. Hydrogen bonding due to the terminal hydroxyl group is therefore presumed to be principally responsible for molecular network formation and as a consequence, gelation [51].

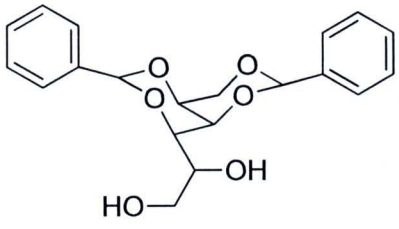


Figure 6 Chemical structure of 1,3:2,4-dibenzylidene sorbitol (DBS) illustrating the unique "butterfly" shape of the molecule [51]

DBS is forms a gel at extremely low concentrations in almost every solvent (polar solvents like ester or non-polar solvents like alkanes) except in water (see illustration in Figure 7) [28]. The gel formation depends upon the type of solvent and the DBS concentration in the solvent. DBS is a chiral amphiphile molecule. In highly diluted solution, the DBS molecule adopts a butterfly conformation. The non-polar benzene wings spread outside the modified sorbitol polar core. The two non-reacted OH-groups from the central core are involved in hydrogen bonds. This molecular architecture is essential to build up stable gel network. Indeed, a 3-D fibrillar network of nearly infinitely long fibers is formed in the gel as can be seen in a bright field electron micrograph of a DBS xerogel prepared directly on the microscope grid (Figure 8) [54]. Although DBS fibers often merge together in bundles, some individual proto-fibers with an average diameter in the range of 10 nm can be observed. The twist along the fibers is linked to the chirality of the molecule.

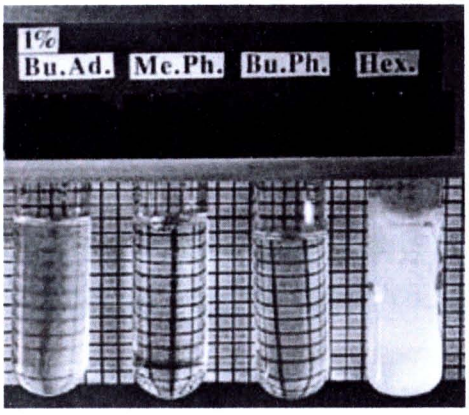


Figure 7 Illustration of the impact of the nature of the solvent on the clarity of DBS gel, (from left to right: butyl adipate, methylphthalate, butylphthalate, hexane)

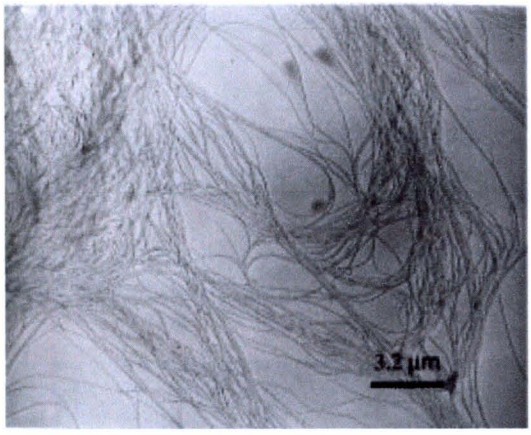


Figure 8 Electron micrographs of Xerogel fibers of DBS, the gel prepared on the microscope grid from a tetrahydrofuran solution, later gelled by addition of benzene

Wilder and co-workers [49] have investigated the composition of such "organogels" as DBS prepared with poly(ethylene glycol) (PEG). Organogels were prepared by dissolving a predetermined amount of DBS in polymer at 200 °C for 10 min and cooled down slowly. Specimens of the DBS/PEG systems for analysis by transmission electron microscopy (TEM) were produced via two different routes. A

nongelled solution with 0.5 wt% DBS was dropped onto a carbon-supported TEM grid and washed repeatedly with toluene to remove residual PEG. And then organogel were cut by hand into thin slices with a razor blade and soaked in distilled water for a period of about 2 weeks to leach out the PEG. It was found that DBS is a low-molar-mass organic gelator that self-organizes on the molecular level and physical gels a wide variety of macromolecule of PEG at low concentration. The gel networks produced in this literature consist of nanofibril measuring between about 10 and 70 nm in diameter (Figure 9).Close examination of this image reveals the existence of fine ("primary") nanofibrils, which are more clearly visible in the higher magnification image provided in Figure 9b. The images in Figure 9c and 9d that confirm peripheral staining of the primary DBS nanofibrils comprising the organogel network. An electrondense feature is circled as a reference marker in Figure 9c and 9d.

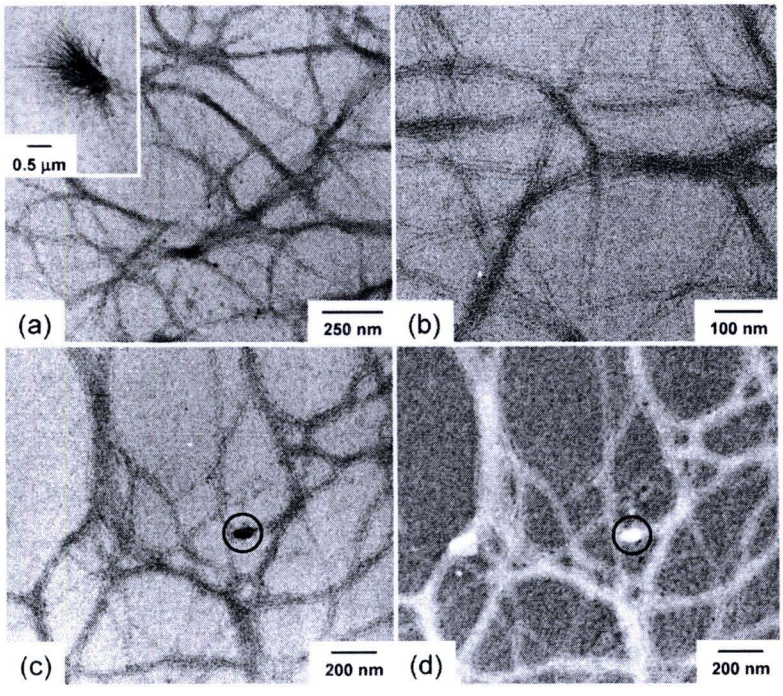


Figure 9 TEM images of PEG/DBS organogel

Effect of DBS on crystallization and melting temperature

As mention earlier, DBS can form a gel in a variety of organic solvents and polymer melts. The addition of small amounts of DBS may also enhance the clarity and reduce haze of solid polymer. Thus, several researches interesting to used DBS as nucleating agent, which shorten the cycle time, improve transparency, physical properties and crystallization temperature by reducing the spherulite size of polymer.

Thierry and co-workers [28] described the polymer crystallization in presence of DBS. When the high temperature homogeneous melt DBS/polymer is cooled down, first the DBS aggregates and constructs a 3-D homogeneous fibrillar network. As the temperature is further reduced, the DBS fibers crystallize and then nucleate the polymer crystallization. This intermediate gel phase has the exceptional advantage to produce a large number of seeds (nuclei) uniformly distributed in the whole polymer matrix. To some extent the foreign additive mimics the self-seeding process. Fibers of 10 nm create a DBS/polymer interface as large as 400 m^2/g of DBS, giving rise to a significant number of nuclei.

Mahaffey and co-workers [55] studied a polyolefin plastic dispersed with additives to improve the mechanical properties and transparency characteristics. The additives used in this work were sorbitol derivatives. These materials were synthesized by reacting sorbitol and benzaldehyde which was substituted in either or both of the *meta* and *para* position with a halogen atom selected from Cl and Br. It was found that the additives can improve mechanical properties and transparency characteristics of polyolefin plastic.

Murai and co-workers [56] explored the synthesis of dibenzylidene sorbitol (DBS) and dibenzylidene xylitol (DBX) in cyclohexane and/or a saturated hydrocarbon having 6-10 carbon atoms were used as a solvent in the reaction. When the reaction progresses, the solvent and water were removed from the reaction by an azeotropic phenomenon to promote the dehydration reaction. The product yields about 70% within about 5-7 hours. Acid catalyst such as sulfuric acid, *p*-toluenesulfonic acid, phosphoric acid, hydrochloric acid, zinc chloride, $C_{2\text{-}12}$ alkyl benzenesulfonic acids, G-acid, L-acid, etc. were used in the reaction usually in about 0.2-3 parts by weight, per 100 parts by weight of sorbitol or xylitol. It was found that the synthesis of di-(p-chlorobenzylidene)xylitol give a yield of product 92% with a purity of 97%.

Shepard and co-workers [11] have studied the addition of a small quantity of DBS to a molten polymer. It was found that DBS may result in a physical gel if conditions permit the DBS molecules to self-organize into a three-dimensional network composed of highly connected nanofibrils. If the polymer crystallizes, DBS may also act as a nucleating agent. It can promote the formation of spherulites, especially in commercially important polyolefins such as polypropylene. Thereafter they examined the thermal and mechanical properties, as well as the morphological characteristics, of an isotactic polypropylene copolymer (iPPe) with 3 wt % ethylene upon addition of less than 1 wt % of 1,3:2,4-di-*p*-methylbenzylidene sorbitol (MDBS) (Figure 10).

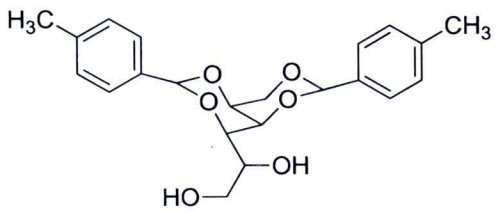


Figure 10 Chemical structure of 1,3:2,4-di-p-methylbenzylidene sorbitol (MDBS)

It was found that both of the complex viscosity (η^*) and crystallization temperature (T_c) are increased when weight percentage of MDBS (W_{MDBS}) 0.18 % wt. Transmission electron micrographs of RuO_4-stained sections confirm the existence of MDBS nanofibrils measuring on the order of 10 nm in diameter and, at higher concentrations fibrillar bundles measuring up to about 200 nm across and several microns in length. The addition of 0.75 % wt MDBS is also found to promote increases in optical clarity, yield strength, tensile strength, and ultimate elongation of modified copolymer. These results indicate that MDBS added to a polyolefin may serve as either a nucleating or clarifying agent at low concentration, or a reinforcing agent at high concentrations.

Feng and co-workers [57] studied the effect of a nucleating agent, dibenzylidene sorbitol (DBS), on the isothermal and nonisothermal crystallization of iPP by DSC. It was also found that the crystallization rate increased with the addition

of DBS because of the increase of nucleation density. Also the crystallization temperature (T_c), increased in the presence of DBS. With an increasing amount of DBS, the crystallization temperature increased (Figure 11)

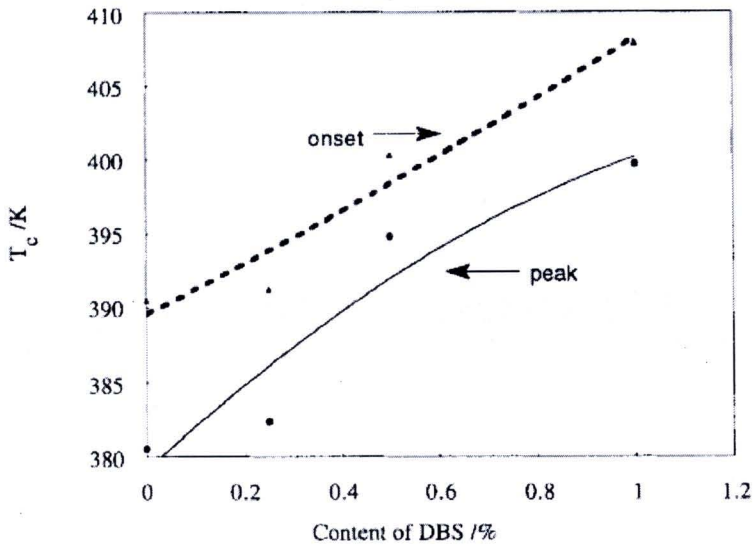


Figure 11 Effect of DBS on the crystallization temperature of iPP

Nagarajan and co-workers [58] investigated the effect of nucleating agents such as dibenzylidene sorbitol (DBS), pine crystal 1500, sodium and potassium benzoates in commercial grade isotactic polypropylene. It was found that DBS can act as a nucleator even at low concentration as 0.014 %wt and the nucleation efficiency of DBS is concentration dependent. The crystallization temperature of isotactic polypropylene (iPP) is linearly proportional to the DBS concentration as seen in Figure 12.

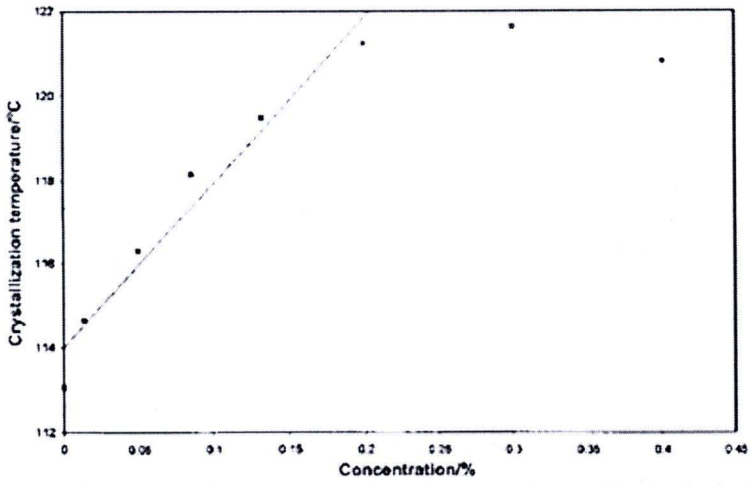


Figure 12 Concentration dependency of DBS on crystallization temperature of iPP

Macro and co-workers [40] investigated the nucleation activity of the di(dimethyl benzylidene)sorbitol (DMDBS) in isotactic-PP(iPP). A series of compositions between 0.025 wt% and 1.5 wt% of the DMDBS were prepared by melt mixing. It was found that the crystallization temperature (T_c) at a cooling rate of 10 °C/min increased with the addition of DMDBS up to 0.3 wt% and then shown plateau up to 1.5 wt% DMDBS. The value of T_c changed from 110 °C for iPP to 128 °C for blends containing 0.3 wt% - 1.5 wt% DMDBS.

Kristainsen and co-worker [10] studied the phase behavior of the system iPP/DMDBS over the entire concentration range and discuss its relevance to the observed clarifying phenomenon. A study of the optical properties of the iPP/DMDBS system reveals that values for haze and clarity of injection molded progressively decrease and increased, respectively. Addition of 0.2-1 wt % of DMDBS in iPP. Figure 13 (top) illustrates this salient effect of the addition of different amount of DMDBS on the macroscopic optical properties of injection molded samples of iPP. Figure 13 (bottom) shows the measured values for clarity and haze for iPP comprising different concentration of DMDBS. Increasing concentration of DMDBS results the clarity of the samples increased and haze decreased up to a critical concentration. The

concentration of samples is higher than 1 wt% of additive showed a decreased clarity and dramatically increased haze.

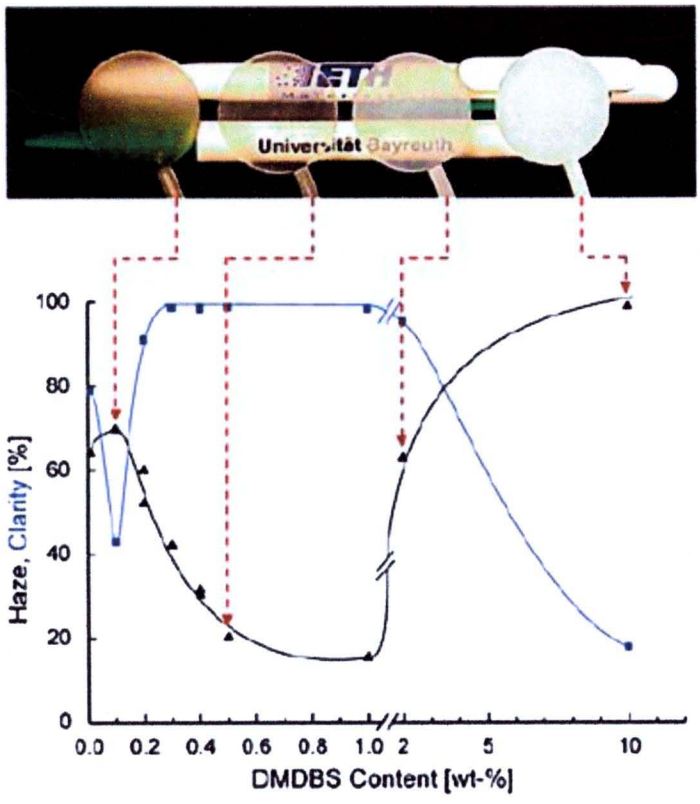


Figure 13 Optical properties of iPP/DMDBS for different amounts of DMDBS. Illustrates viewed through injection molded plaques containing 0.1, 0.5, 2, and 10 % wt of DMDBS (top) and measured values for haze (▲) and clarity (■) as a function of the DMDBS content (bottom)

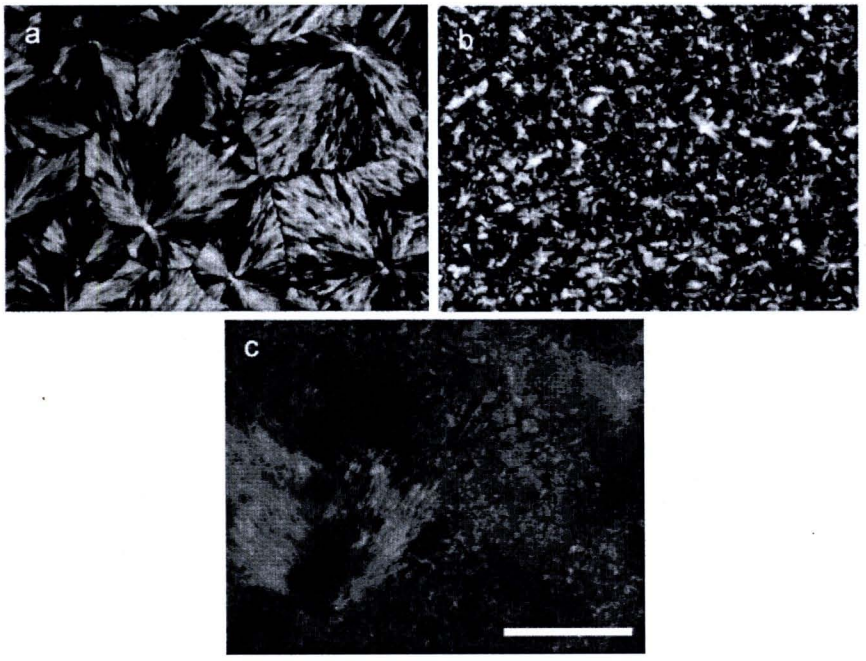


Figure 14 Optical micrograph of the morphology of compression molded film of binary i-PP/DMDBS mixtures containing different amounts of DMDBS (in wt %): (a) 0.1, (b) 0.2, (c) 40.0. Scale bar 100 μm

Figure 14 are optical micrographs show different binary mixtures after cooling from the melt to room temperature at a rate of 10 °C/min. At DMDBS concentration levels of up to about 0.1 wt% (Figure 14a) the sphereulite size of i-PP was found to be approximately the same as in neat i-PP. As is well known, at a DMDBS concentration of 0.2 wt%, a very dramatic decrease in polymer spherulite size was observed (Figure 14b). At DMDBS concentrations of more than 5 wt% the appearance of the mixtures was dominated by the presence of large, crystalline DMDBS domains, and only a few polymeric spherulite structures could be distinguished (Figure 14c).

Cao and co-workers [59] studied the effect of different concentration of DBS on the crystallization temperature (T_c) of iPP. It was found that the DBS was an excellent nucleating agent for iPP, resulting in a significantly increase of crystallization temperature and decrease of crystal dimension.

Effect of DBS on mechanical properties and control orientation of polymers

The physical properties of the final product depend on the resultant microstructure. One particular class of microstructure involves the generation of globally anisotropic texture in which there is a strong preferred orientation of the structural elements, such as crystal lamellae, domains, or molecular segments, which is often is produced through flow fields [60].

Lipp and co-worker [8] investigated the role of 1,3:2,4-di(3,4-methylbenzylidene)sorbitol (DMDBS) in inducing oriented crystallization during the melt spinning of PP fiber. Two temperature protocols (TP) were used, differing in the temperature at which TP1 the melt was held in the piston: 10 min at 220 °C (in order to dissolve DMDBS in the melt) under contact pressure and subsequently a decrease to 180 °C for the spinning process. While the sample for TP2 were heated to 180 °C and kept at constant temperature, in order to keep the DMDBS fibrillar structure, formed within PP during the compounding step. The results show a higher tensile modulus at 0.4 % wt of DMDBS, likely due to better orientation of the PP crystals along the fiber direction (Figure 15).

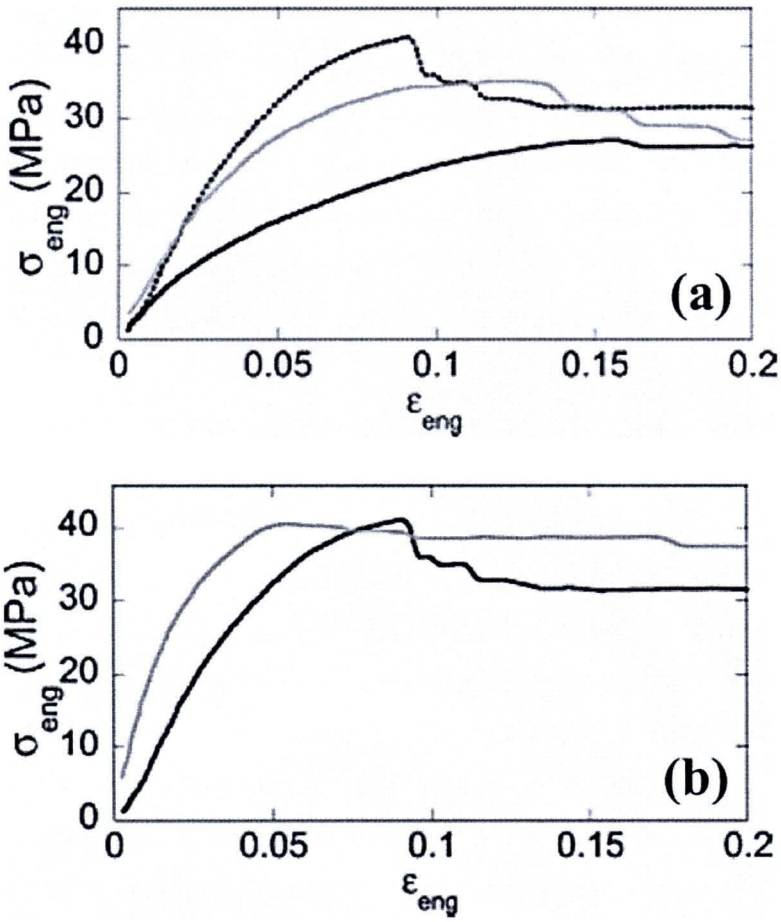


Figure 15 (a) Stress-strain curves measured for fibers fabricated using TP2 with low SDR, where the solid black, the gray, and dashed lines were taken for 0, 1 and 0.4% DMDBS, respectively. (b) Stress-strain curves measured for fibers, containing 0.4% MDBS, fabricated using TP2, where the black and gray lines indicate, low and high SDR, respectively

Many studies have been carried out to investigate the molecular orientation and resultant morphology under different shear-flow conditions. It is interesting to find that a nucleating agent could not only increase the crystallization temperature and decrease the crystal size, but also improve the overall orientation of polymer [61]. The application of extension flow to a polymer melt can lead to a significant level of chain extension and orientation, and for crystallisable polymer, the subsequent

crystallization may lead to a substantial amplification of the level of preferred molecular orientation present in the melt [19]. Polymer melts under shear can exhibit many important macroscopic effects including flow-dependent viscosity, higher normal stresses, enhanced nucleation and crystallization rate, and shish-kebab (cylindrite) morphology formation. The study of the crystallization process of polyolefins from melt under shear can provide fundamental knowledge in order to control the morphology and properties of products obtained from various processing conditions [62].

Since the low-molar-mass self-assembled nanoparticles play the part of the extended chains. A flow field is used to generate a high level of preferred orientation of extended nanoparticles dispersed in the polymer melt. On cooling, the aligned nanofibrils direct the subsequent crystallization to yield a material with a high level of lamellar alignment [15]. The influence of DBS and it derivatives on the orientation achieved during processing of semi-crystalline polymers has also been investigated. Enhancement of shear-induced orientation by the presence of DBS fibrils was indicated [12-15]. The fibrils align parallel to the applied shear while polymer crystals grow epitaxially on the fibril surface, perpendicular to the shear direction [15].

Nogales and co-workers [12] presented a novel and method of microstructure control in polyolefins by dispersing tiny amount of sorbitol derivatives (1wt %) in the polymer (copolymer containing PP and PE (CPP) and linear PE). The subsequent crystal growth can be controlled with modest prior flow-fields. Molten samples were held at temperature above the calorimetric melting point of the polymer and subjected to a controlled shear flow. The shear flow was rapidly reduced to initiate polymer crystallization. Under shear flow, the additive forms highly extended crystals which lie parallel to the flow-field and which serve to direct the crystallization of the polymer leading to a massive amplification of the anisotropy present in the melt. The strong anisotropy in the modified samples as compare to the isotropic samples in the non-modified specimens is shown in Figure 16.

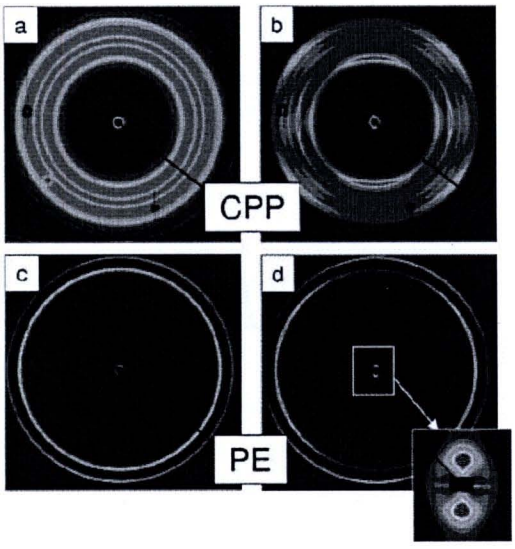


Figure 16 Templating the orientation through crystallization. WAXS patterns showing the effect of the DBS on the crystal orientation distribution of the semi-crystalline polymers. (a) and (c) are the non-modified CPP and PE. (b) and (d) are the DBS-modified CPP add PE. In (d) the inset shows the SAXS pattern for the same sample

In the same year [13], they have studied the effects in propylene/ethylene copolymer (cPP) systems containing different amounts of DBS by using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) techniques. It was found that higher 0.5 wt% of DBS, there is saturation in crystallization temperature (T_c), indicating that the addition of more DBS is not effective in increasing the T_c of cPP.

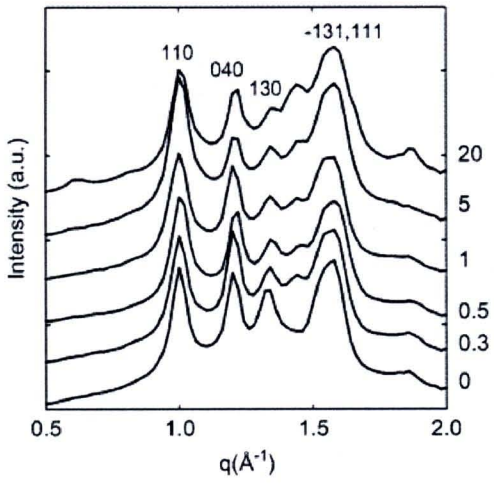


Figure 17 Plots showing wide angle X-ray scattering intensity as a function of $|q|$ for the system under investigation. The label to the right of each trace indicate the percentage DBS

Figure 17 shows WAXS patterns obtained from polypropylene copolymer samples containing different concentrations of DBS. These features indicate that the crystalline structure of the sample corresponds to the α-form of isotactic polypropylene [63]. This demonstrates that the polymer's unit cell is not significantly modified by the presence of the nucleating agent.

Wangsoub and co-workers [15] show the small quantities of DBS in poly (ε-caprolactone) coupled with shear flow provide a self-assembling nanoscale framework to yield high level of crystal orientation. During modest shear flow of the melt, the additive forms highly extended nanofibrils which adopt a preferred alignment with respect to the flow field. Figure 18 shows a compilation of the SAXS and WAXS patterns for the four combinations of PCL and DBS, no shear and shear taken at equivalent point during the processing cycle.

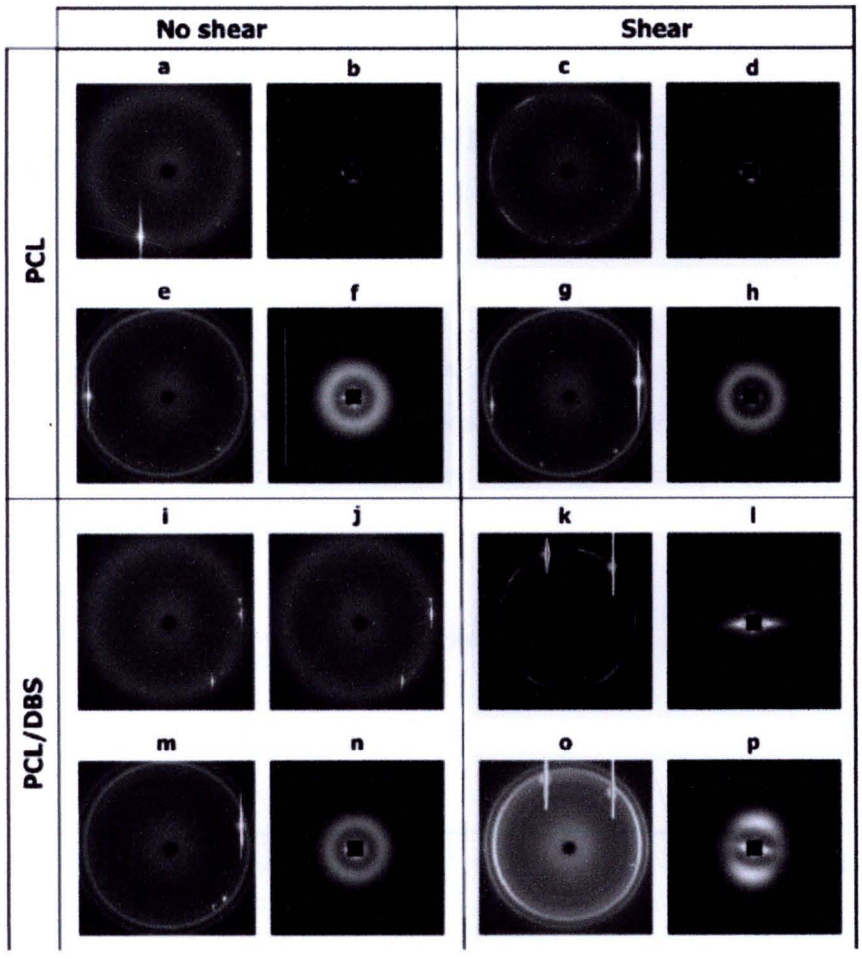


Figure 18 WAXS and SAXS patterns obtained for samples of PCL and 3 % DBS/PCL samples at the same point of the thermal and shear flow cycle. Each set of pattern is organized as a aquare block of four, representing WAXS and SAXS, during shear in the melt, and WAXS and SAXS at room temperature after crystallization. (a), (b), (e) and (f)-PCL with no shear; (c), (d), (g) and (h)-PCL with shear; (i), (j), (m) and (n)-DBS/PCL with no shear; (k), (l), (o) and (p)-DBS/PCL with shear. The flow direction is vertical