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# Halogenated Sorbitol Derivatives Using as Nucleating Agent and Their Effect on Orientation of Polypropylene Fiber

**Thanita SUTTHATANG, Uthai WICHAI and Supatra WANGSOUB***

*Department of Chemistry, Naresuan University, Phitsanulok, 65000 Thailand*

## Abstract

In this work, two halogenated derivatives of benzylidene sorbitol were synthesized by reacting D-sorbitol with an aromatic aldehyde in the present of an acid catalyst. ie.chloro and bromo derivatives for using as nucleating agent for polypropylene. For chloro derivative, different positions of substituent (ortho, meta and para) were also synthesised. SEM and TEM micrographs of gel extracted from organic solvent revealed long fibril network of chloro and bromo substitutes which their diameters are in the range of about 10-200 nm. Small amount (0.1-1%wt) of these materials was blended with isotactic polypropylene (iPP) by two roll mill machine and the mixture was made to fiber form by extrusion. It was found that these fibrils formed in polymer melt and shear flow during fiber preparation process. The effect of fiber preparation conditions such as die temperature, screw speed and crystallization rate on crystal orientation of polypropylene were studied. The effect of halogenated sorbitol derivatives on the crystallization of iPP were studied using different scanning calorimeter technique. It was found that 0.5 wt% of para chloro derivative show the most effective as a nucleating agent for iPP compared to the other substitution positions. The crystallization temperature of iPP containing 0.5 wt% of para chloro sorbitol increases up to 15% compared to the crystallization of neat PP. The para bromo shows less effective in an increasing the crystallization temperature when compared to the para chloro. No further increase in the crystallization temperature when the amounts of all derivatives are higher than 0.5%wt. It was found that the beta structure of iPP can be changed to alpha structure when small amount of sorbitol derivatives are presented below their solubility temperature.

**Key words:** Fibril morphology, Sorbitol derivatives, Polypropylene, Nanostructure

## Introduction

Polypropylene (PP) is a semi-crystalline polymer that is different in stereospecificity and comonomer content. It is commercially produced in isotactic, syndiotactic, and atactic forms with varying degree of tacticity, the isotactic form being the most common. Depending on the solidification, PP can crystallize into four different crystal polymorphs, α (monoclinic), β (hexagonal), γ (triclinic) and a smetic form.(1-4) PP is widely used in many applications due to its excellent balance of physical properties and low cost. The property profile of PP is strongly influenced by the level of crystallinity that is achieved when the polymer crystallizes from the melt. When molten PP cools during extrusion or injection molding, crystals form at nucleation sites, which are often impurity particles. These crystals radiate outward from these nucleating centers forming spherical structure known as spherulite. Eventually the spherulites impinge on one another and the part become fully solid in nature. Amorphous (non-crystalline) material is also entrained within the spherulite, so that the overall crystallinity of the final part is somewhere in the range of 40% to 60% crystalline. The modulus (stiffness) and strength of the final part is depending on the percent crystallinity, and higher crystallinity leads to higher stiffness and strength.(5)

1,3:2,4-dibenzylidene sorbitol (DBS) is a butterfly-shaped amphiphile derived from the sugar alcohol D-glucitol. It is known as a gelator. It can self-organize to form a 3D network, stabilized by hydrogen bonds at relatively low concentrations in a variety of organic solvents and polymers, to produce organogels.(6) Several DBS have been studied as organogels to improve mechanical properties, transparency and crystallization temperature. Mahaffey(7) studied a polyolefin plastic dispersed with additives to improve 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

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* Corresponding author: E-mail: supatraw@nu.ac.th

atom selected from Cl and Br. It was found that the additives can improve mechanical properties and transparency characteristics of polyolefin plastic. Nagarajan et al.[8] 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 act as a nucleator event at low concentration as 0.014 %wt and the nucleation efficiency of DBS is concentration dependent. The crystallization temperature of isotactic polypropylene is linearly proportional to the DBS concentration. Shepard et al.[9] examined the thermal and mechanical properties, as well as morphological characteristics, of iPP copolymer with 3 wt% ethylene upon addition of less than 1 wt% of 1,3:2,4-di-*p*-methylbenzylidene sorbitol (MDBS). The addition of MDBS at different concentrations is also found to promote increase in optical clarity, yield strength, tensile strength, and ultimate elongation of modified copolymer formulations. Lipp et al.[10] 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. The results show a higher tensile modulus at 0.4% DMDBS, likely due to better orientation of the PP crystals along the fiber direction.

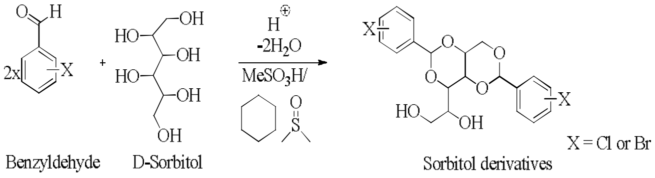
In this work, the effect of addition halogenated sorbitol derivatives using as nucleating agent and their effect on orientation of polypropylene fiber were investigated. Sorbitol derivatives were prepared by acid catalyses reaction of D-sorbitol with an aromatic aldehyde in cyclohexane. Sorbitol derivatives were characterized by FTIR spectroscopy, NMR spectroscopy and DSC techniques. The iPP containing sorbitol derivatives were prepared by melt blending process using two roll mills. DSC and optical techniques were used to study the efficiency of all sorbitol derivatives as a nucleating agent for polypropylene. SAXS and WAXS were used to investigate the crystal orientation of polypropylene and preferred orientation of polypropylene lamellar.

## Materials and Experimental Procedures

### Materials

Polypropylene used in this work is isotactic polypropylene (iPP) under the trade name of Mophen HP400H from Basell Polyolefins in an extrusion grade polypropylene homopolymer. The melt flow index and density are 2 g/10 min (230°C/2.16 kg) and 0.9 g/cm$^3$, respectively.

DBS derivatives were prepared by the acid catalyses reaction of D-sorbitol with an aromatic aldehyde (ie.chloro and bromo-benzaldehyde) in cyclohexane. For chloro derivative, different positions of substituent (ortho, meta and para) were also synthesised. The procedure for sorbitol derivatives synthesis were shown in Scheme 1.



**Scheme 1**. Synthesis of sorbitol derivatives

### Melt Blending

Isotactic polypropylene (iPP) and halogenated sorbitol derivatives were melt-blended using two-roll mill at 140°C for 5 min. The compounds were then compressed with hot press mold into film thickness 2 mm using mold temperature at 175°C for 5 min.

### Differential Scanning Calorimetry (DSC)

The samples were placed in aluminum pan about 10 to 15 mg of each sample. The samples were heated from 25°C to 180°C with heating rate of 10°C/min, and then cooled down from 180°C to 25°C with cooling rate 5°C/min, and reheated again with heating rate of 10°C/min.

### Fiber Preparation

The process used a mini-extruder (Randcastle RCP-0625) equipped with a fiber line having a single hole spinneret (Figure 1). An aluminum tube was connected with the die to retain a temperature inside during the process. The temperature profiles were fixed at 123, 180, 190, and 225°C for feed zone, compression zone, metering zone, and die, respectively. The processing condition for fiber forming was shown in Table 1. Neat iPP and iPP/sorbitol derivatives pellets were fed into the hopper of mini-extruder to melt the pellet. The molten polymer was extruded through the spinneret and become an extrudate or as-spun fiber was pulled by slow set of rotating godets, immediately cooled in air and subsequently cooled in water. After the as-spun fiber was passed through water bath, it was continuously fed into a glycerol bath set as 95°C.

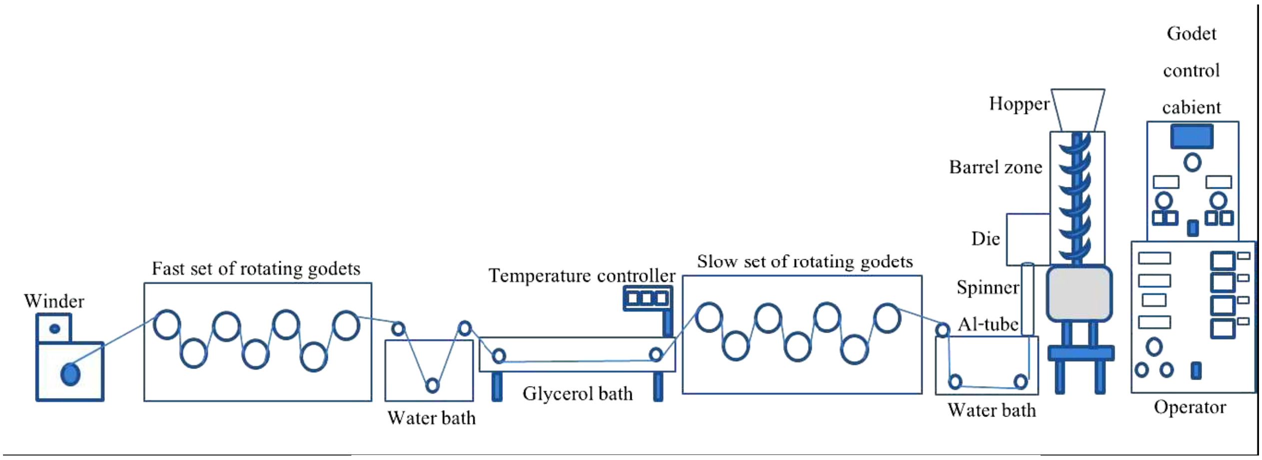


**Figure 1.** Schematic of mini-extruder and fiber line diagram

**Table 1.** Extrusion condition for sample preparation of neat iPP fiber and iPP/halogenated sorbitol derivatives fiber

| Screw temperature (°C) with screw speed 2 rpm | | | |
|---|---|---|---|
| Feed zone | Compression zone | Metering zone | Die |
| 123 | 180 | 190 | 225 |

### *Small- and Wide-Angle X-ray Scattering (SAXS and WAXS)*

Time resolved X-ray scattering measurements were performed on beam-line BL2.2: SAXS at Siam photon laboratory, Synchrotron light research institute (Public organization) (Nakhon Ratchasima, Thailand), using a beam 0.2 mm in diameter. X-ray scattering data were collected using a CCD (Mar165) X-ray detector and photon energy was operating at 8 keV. The detector was located at a distance from the sample of 250 cm for small-angle X-ray scattering experiments and of 14 cm for wide-angle X-ray scattering experiments. The integration times for most samples were 300 s.

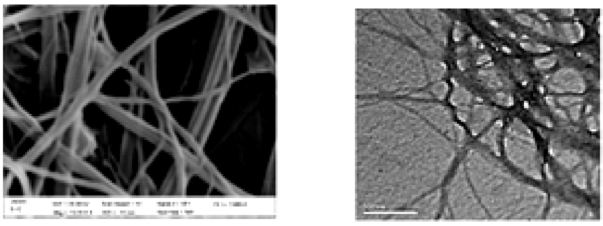
## Results and Discussion

### *Fibril Morphology*

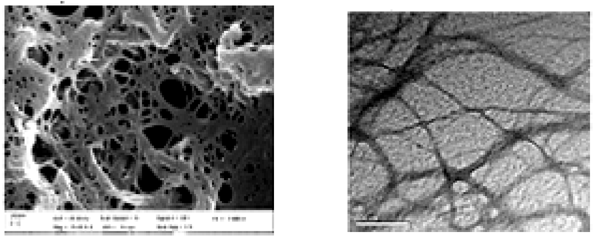
The physical gel of sorbitol derivatives were prepared by dissolving various concentrations (0.05-0.2 % wt) in alkanes at elevated temperature until the mixture becomes a clear solution. After that the homogeneous solution was cooled down to room temperature. SEM and TEM techniques were used to investigate the fibril morphology of sorbitol derivatives. Figure 2 shows SEM and TEM which were dissolved in dodecane. It can be seen micrographs of extracted of sorbitol derivatives that all sorbitol derivatives are in the form of fibril bundle and twisted in low molecular weight solvent.

SEM micrographs TEM micrographs

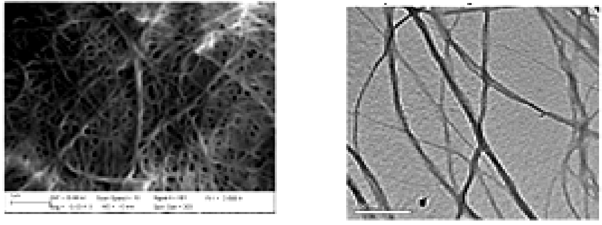
a) 0.2%*o*-Cl-DBS b) 0.1% *o*-Cl-DBS



c) 0.2%*m*-Cl-DBS d) 0.1% *m*-Cl-DBS



e) 0.2%*p*-Cl-DBS f) 0.1% *p*-Cl-DBS



g) 0.2%*p*-Br-DBS h) 0.1% *p*-Br-DBS

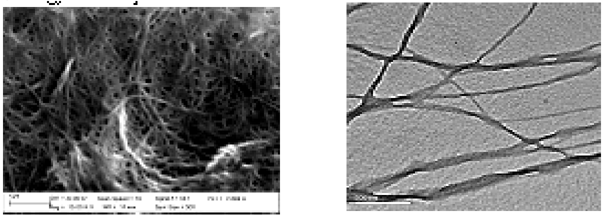


**Figure 2.** SEM and TEM micrographs of sorbitol derivatives in dodecane

It was found that the different lengths of alkane chain has no effect on diameter and length of these fibrils. In case of low concentration, i.e. 0.05% wt of *o*-Cl-DBS and *m*-Cl-DBS, the fibril network could not be observed by TEM and SEM techniques. Therefore, the concentration of *o*-Cl-DBS and *m*-Cl-DBS were increased up to 0.1 and 0.2% wt, respectively. It was found that the fibril network can be revealed and theirs diameters are similar to those of *p*-Cl-DBS and *p*-Br-DBS.

### *Effect of Sorbitol Derivatives on Crystallization Temperature of Polypropylene*

Figure 3 and Table 2 show cooling thermogram of crystallization temperature ($T_c$) of iPP and iPP containing the same amount of chloro derivatives (0.5 % wt) by two-roll mill. It can be seen that *o*-Cl-DBS and *p*-Cl-DBS show more effective in term of increasing the crystallization temperature ($T_c$) of iPP. In term of type, the chloro derivatives show an increasing in the crystallization temperature of iPP more than bromo derivative.

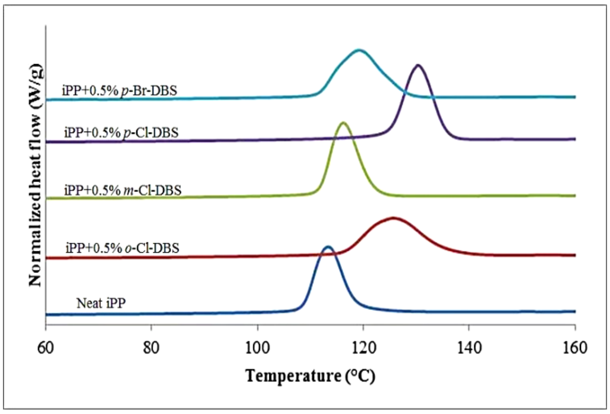


**Figure 3.** Cooling thermograms of neat iPP and iPP containing 0.5 %wt of sorbitol derivatives by two-roll mill

**Table 2.** Crystallization temperature of neat iPP and iPP containing 0.5 %wt of sorbitol derivatives

| Sample | Crystallization temperature (°C) | |
|---|---|---|
| | Onset | Peak |
| Neat iPP | 118.78 | 114.04 |
| iPP/0.5%*o*-Cl-DBS | 133.24 | 124.59 |
| iPP/0.5%*m*-Cl-DBS | 122.52 | 117.46 |
| iPP/0.5%*p*-Cl-DBS | 136.42 | 131.61 |
| iPP/0.5% *p*-Br-DBS | 127.99 | 114.04 |

The cooling thermogram of neat iPP and iPP containing different amounts of *p*-Cl-DBS by two-roll mill were shown in Figure 4. It can be seen that the addition of 0.5 %wt of *p*-Cl-DBS increases the crystallization temperature ($T_c$) of iPP. At concentration higher than 0.5 %wt, it is likely that the crystallization temperature ($T_c$) of iPP contained *p*-Cl-DBS remain constant as shown in Figure 5.

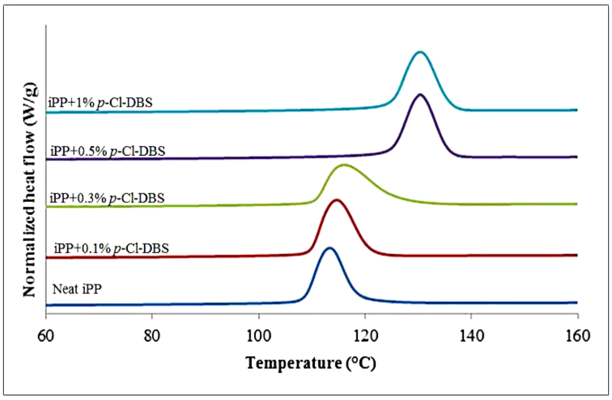


**Figure 4.** Cooling thermograms of neat iPP and iPP containing different amounts of p-Cl-DBS by two-roll mill

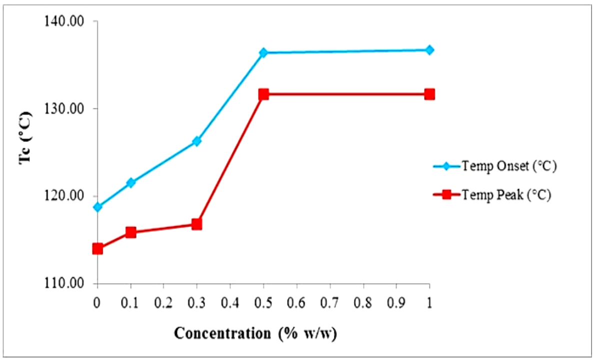


**Figure 5.** Crystallization temperature of neat iPP and iPP containing different amounts of p-Cl-DBS by two-roll mill

### *Effect of Sorbitol Derivatives on Melting Temperature of Polypropylene*

Figure 6 shows the melting thermograms of neat iPP and iPP containing different amounts of *p*-Cl-DBS. The effect of amount of sorbitol derivatives on the melting temperature ($T_m$) of iPP was shown in Figure 7. It was found that the melting temperature ($T_m$) observed of *p*-Cl-DBS in iPP remain more or less constant with various amount of additives.

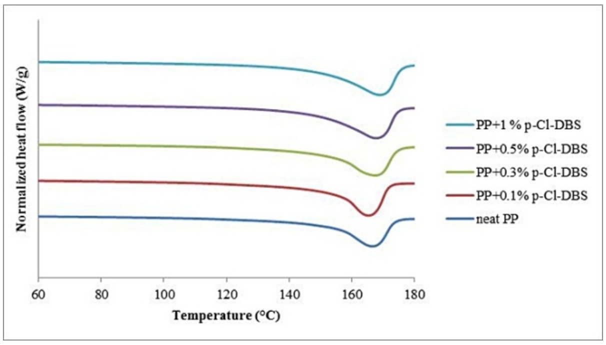


**Figure 6.** Melting thermograms of neat iPP and iPP containing different amounts of p-Cl-DBS

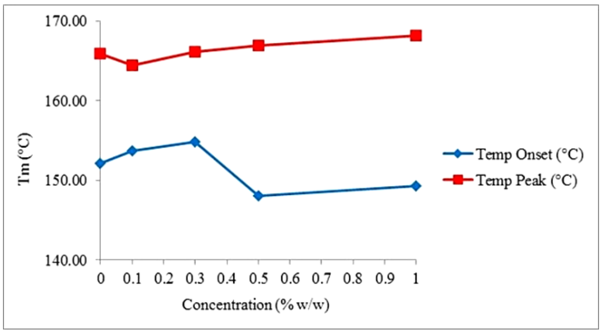


**Figure 7.** Melting temperatures of neat iPP and iPP containing different amounts of p-Cl-DBS

The data in Figure 8 derived from the second heating thermograms of neat iPP and iPP containing 1%wt of sorbitol derivatives. The samples were heated and cooled in the same condition as shown in Figure 6. It can be seen that the addition of 1% wt of sorbitol derivatives are not effecting on the melting temperature of iPP.

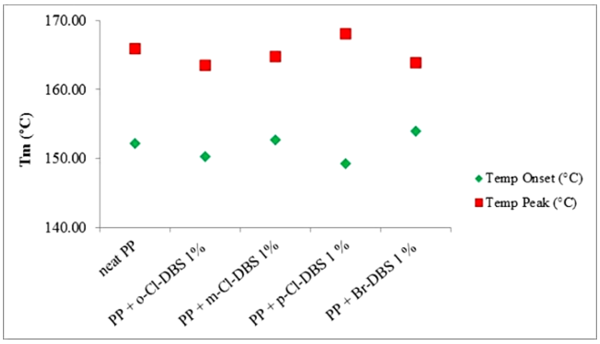


**Figure 8.** Melting temperatures of neat iPP and iPP containing 1% wt of sorbitol derivatives

## *Effect of Sorbitol Derivatives on Nucleation of Polypropylene*

The effect of sorbitol derivatives on spherulite size of iPP were observed by optical microscopy technique. Figure 9 shows spherulite structures of neat iPP and iPP containing sorbitol derivatives. Figure 9a demonstrates the spherulite of neat iPP about 100 µm which, was clearly seen. The addition of 0.1% wt of sorbitol derivatives into iPP was not clearly seen the different of spherulite size, but it is smaller than that of neat iPP (not show here).

The spherulite of iPP containing 0.5% wt of *o*-Cl-DBS and *m*-Cl-DBS are still large. The addition of 0.5% wt of *p*-Cl-DBS and *p*-Br-DBS (Figure 9d and 9e) show a very dramatic decreasing in spherulite sizes of iPP corresponding to the result from DSC. Especially, the spherulite sizes of iPP containing 0.5% wt of *p*-Br-DBS (Figure 9e) are very small and regular compared to the other derivatives. This result is consistent with the crystallization temperature and degree of crystallinity of iPP as mentioned above. Meanwhile, this is similar to the studying of Kristainsen(11) by adding 0.2-1% wt of DMDBS in iPP for study optical property.

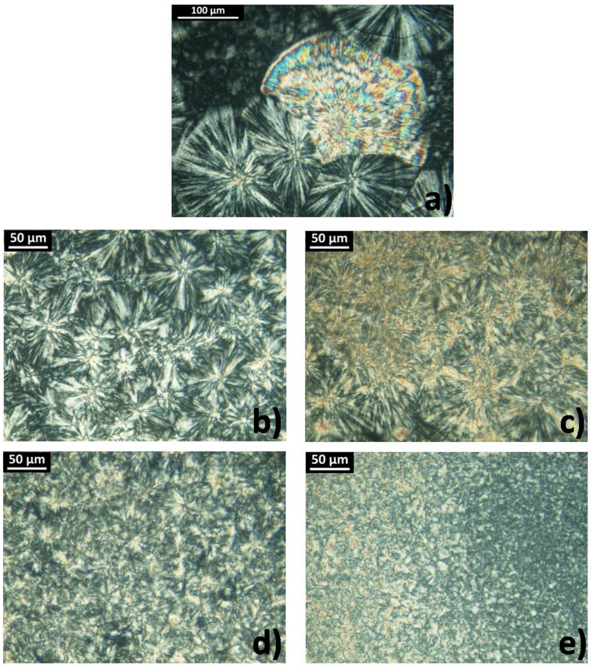


**Figure 9.** Optical micrographs of a) neat iPP b) iPP/ 0.5%o-Cl-DBS c) iPP/ 0.5%m-Cl-DBS d) iPP 0.5%p-Cl-DBS and e) iPP/0.5%p-Br-DBS

## *Effect of Sorbitol Derivatives on Orientation of Polypropylene*

In this work, the blend samples were spun into fiber form under the flow field during extrusion process. The sorbitol derivatives act as a nucleating agent and may direct the crystallization of polypropylene crystal. This templating process will give high orientation of polymer crystal.

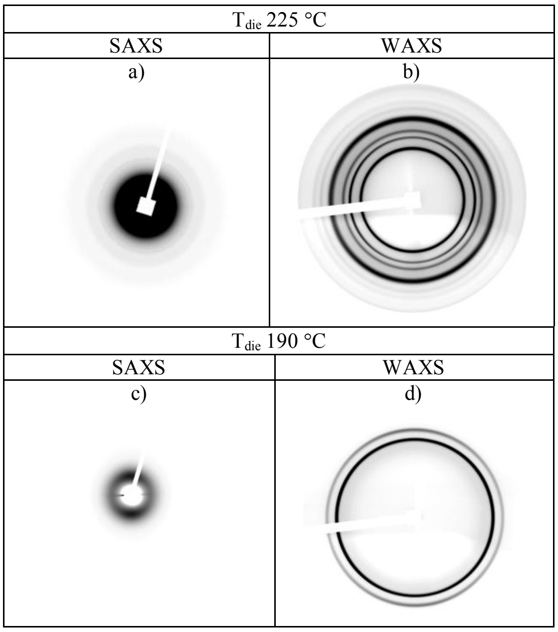


**Figure 10.** SAXS and WAXS patterns of neat iPP fiber at different die temperatures screw speed 2 rpm

SAXS and WAXS patterns of as-spun neat iPP at die temperature 225°C in Figure 10a and 10b show no preferred orientation. When the die temperature is decreased (190°C) WAXS pattern of as-spun neat iPP shows an isotropic distribution of intensity throughout the crystallization. It is indicating that at this condition the crystal are randomly oriented. Conversely, it is clearly seen that the crystal structure is changed as seen in Figure 10b and 10d. While, the SAXS pattern at low die temperature (190°C) shows low level of preferred orientation (Figure 10c).

Many researchers demonstrate the oriented crystal development in iPP under shear flow. It was found that the diffraction peaks of the monoclinic α-phase at the scattering angles 2θ of 14°C (110), 16.9°C(040), 18.5°C (130), 21.3°C (111), and 21.8°C (131 and 041) [12-17]. The hexagonal β-iPP modification can be observed at the scattering angles 2θ = 16°C (300) and 21°C (301). Figure 11a also presents a plot of scattered intensity as a function of scattering angle (2θ). The crystal modifications of as-spun neat iPP fiber at die temperature 225 °C which were characterized with WAXS correspond to their crystal modifications of research above. In the case of as-spun neat iPP at die temperature 190°C, this pattern may be the reflection plane (301) (at the scattering angles 2θ = 21.4°C) of β-phase. This sample could not be clearly identified. It is due to Bragg reflection plane (300) of as-spun neat iPP at die temperature 190 °C absent, which could not be found from the others. The β-form can be obtained by specific sample preparation conditions, such as the presence of heterogeneous nucleating agents, crystallization in a temperature gradient or crystallization under shear.

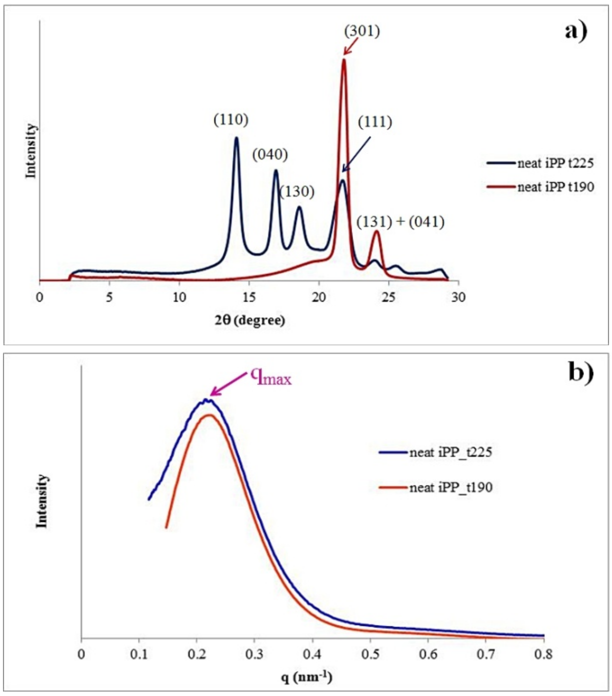


**Figure 11.** a) Equatorial sections of WAXS Patterns b) Meridional section of SAXS of neat iPP fiber at different die temperatures

**Table 3**.q- and d-space of iPP as-spun fiber at different die temperatures at screw speed 2 rpm

| $T_{die}$ | q ($nm^{-1}$) | d-space (nm) |
|---|---|---|
| 225 °C | 0.2166 | 28.9935 |
| 190 °C | 0.2179 | 28.8206 |

Table 3 shows the long period 28.9935 nm of neat iPP ($d = 2\pi/q_{max}$) at die temperatures 225°C, for die temperature 190 °C the long period is about 28.8206 nm. It demonstrates that the long period of neat iPP in both processing temperatures are not changed. Die temperature indicates no effect on long period of neat iPP which is similar to the study of Kumaraswamy et al.(18) The influence of shearing condition has been examined (examine section along the direction perpendicular to flow, *F* and along the lobes from the daughter lamellae, *D*) on the development of semicrystalline morphology in iPP by using in-situ synchrotron X-ray scattering. The value of long spacing ($L_B$) obtained from an analysis of the F section ($L_{B,F}$ = 28 nm) is similar to that from an analysis of the D direction $L_{B,D}$ = 28.9 nm.

Figure 12 shows wide-angle X-ray patterns obtained from as-spun neat iPP fiber and iPP fiber containing 0.5% wt of sorbitol derivatives at die temperature 190°C. It can be clearly seen that the iPP fiber containing 0.5% wt of sorbitol derivatives show the α-crystal reflections, while neat iPP reveals another crystal reflections (here, it may be β-form). When the die temperature increased up to 225°C and amount of sorbitol derivatives increased to 1% wt, it can be seen that the WAXS patterns of iPP with and without sorbitol derivatives are similar as seen in Figure 13.

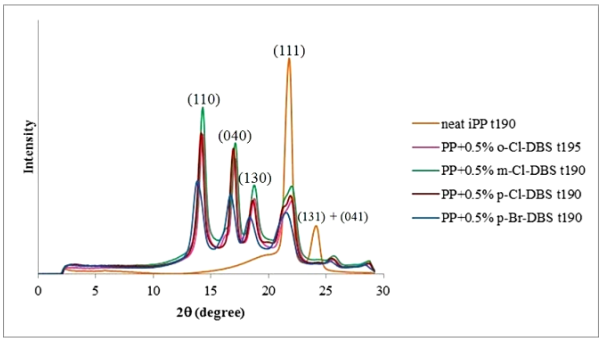


**Figure 12.** Equatorial sections of WAXS patterns of neat iPP and PP/0.5% wt of sorbitol derivatives at die temperature 190 ºC

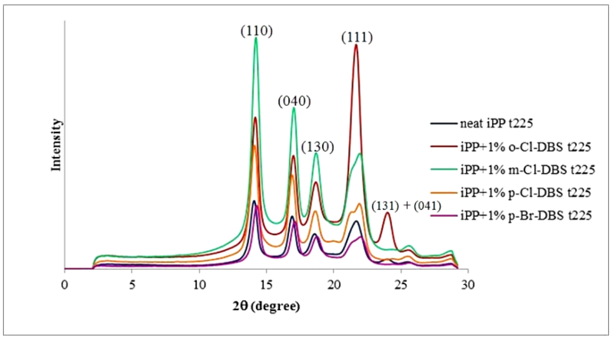


**Figure 13.** Equatorial sections of WAXS patterns of neat iPP and PP/1% wt of sorbitol derivatives at die temperature 225ºC

## Conclusions

SEM and TEM micrographs of gel extracted from organic solvent revealed the fibril network of chloro and bromo dibenzylidene sorbitol derivatives which their diameters can be observed in the range of about 10-200 nm. The crystallization temperature of iPP containing 0.5 wt% of para chloro sorbitol increases up to 15% compared to the crystallization of neat PP. The para bromo shows less effective in an increasing the crystallization temperature when compared to the para chloro. No further increase in the crystallization temperature when the amounts of all derivatives are higher than 0.5%wt. Therefore, these materials are able to use as a nucleating agent for iPP. The high level of preferred orientation of iPP lamellar is clearly seen when the samples were dispersed with 0.5% of sorbitol derivatives under low processing temperature where the fibril still exist in the polymer melt. The beta structure of iPP can be changed to alpha structure when small amount of sorbitol derivatives are presented below their solubility temperature.

## Acknowledgements

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