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Development of highly oriented polymer crystals from row assemblies

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Abstract

The development of organized structures from sheared isotactic polypropylene melts with different amounts of dibenzylidene sorbitol (DBS) as a nucleating agent has been followed in real time using small angle X-ray scattering in conjunction with synchrotron radiation. The results show that, above a certain DBS concentration threshold, the lamellar crystals are highly oriented perpendicular to the direction of the prior applied shear field. The role of the directing agent in nucleating the crystallization and templating the crystal anisotropy is discussed.

Keywords: Nucleating agent; Shear; Polypropylene

1. Introduction

The morphology of a semicrystalline polymer depends substantially on aspects such us the processing conditions and the composition of the system. Processing a crystallizable polymer material implies in general, the application of deformation fields. In many cases, due to the viscoelastic nature of polymer melts, memory of the melt deformation will show up in the crystallized material. For example, elongational flow results in the extension of some of the polymer chains, which act as row nuclei during crystallization. Under these conditions, shish-kebabs structures are usually observed [1], with chain folded lamellae growing, to a first approximation, perpendicular to the row nuclei. The existence of these organized structures is not exclusive of the elongational flow. Several investigations show that shear flow may produce orientation in the polymer melt, which templates the subsequent crystallization [2–6]. The orientation in the semicrystalline material is therefore, directly related to the orientation in the polymer melt induced by the flow field. This melt orientation may depend on many factors, such as the nature and intensity of the applied flow, the processing temperature or the molecular characteristics of the polymeric material. It is clear that the molecular weight distribution of the system plays a very important role. Recently, the orientation in the crystallized material has been shown to depend strongly on the presence of small fractions of long molecular chains [7,8]. The way in which the extended long molecules nucleate the crystallization of the bulk material is a matter of considerable discussion [7,8]. Another important factor in polymer processing is the addition of low molecular weight compounds that may modify the characteristics of the crystallized polymer system. The presence of a particular nucleating agent may change radically the behaviour of the system under flow. Nucleating agents increase the rate of crystal nucleation providing heterogeneous nucleation sites. In particular, compounds based on sorbitols are particularly efficient [9]. When sorbitol derivatives are dispersed into a polymer matrix they self-assemble into fibrous structures that appear to act as nucleation centres for polymer crystals [10]. In isotactic polypropylene (iPP), they are used as clarifying agents since they increase considerably the nucleation density yielding to smaller spherulites [11]. Recently we have reported that highly oriented systems can be obtained by adding small amounts of DBS to iPP, that otherwise would form randomly distributed crystals when deformed and crystallizing under the same conditions [12,13]. The explanation for that is based on a model where, in the polymer melt, below a certain temperature, the DBS form a gel consisting on a fibrous network, that acts as a template for the polymer crystallization.

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Synchrotron based X-ray scattering methods allow real time studies of structural changes in crystallizing polymers. The high flux of these sources offers the possibility of coupling scattering techniques with complicated sample environments [14]. The aim of the present investigation is to study the formation of highly anisotropic semicrystalline structures in polypropylene from sheared polymer melts with presence of DBS as a nucleating agent. We have exploited synchrotron small angle X-ray scattering techniques in conjunction with a shear cell developed specifically for this purpose, for in situ studies of the development of this highly oriented morphology.

2. Experimental part

The polymer system examined in this study is a polypropylene/ethylene copolymer, with trade name NOVOLEN (BASF plc.). The ethylene content is about 3% according to infrared spectroscopy [15]. The nucleating agent dibenzylidene sorbitol (DBS) was obtained from Milliken under the trade name of Millad 3905. It was added to the polypropylene matrix by solution–precipitation method. The precipitated solution was then filtered and allowed to dry for several hours. Final removal of the solvent was done by vacuum drying at 70 °C. The compounded sample obtained in such a way was then melt pressed at 190 °C in the shape of discs of 1 mm thickness and 18 mm in diameter, suitable for use in the shear experiments. The samples are referred in this work as iPP*x*, where *x* indicates the percentage in weight of DBS in the sample.

Time resolved measurements were performed on beamline 16.1 at the synchrotron radiation source at Daresbury (Cheshire, UK), using a beam ($\lambda = 1.488$ Å) of ~0.4 mm diameter. Small angle X-ray scattering data were collected using the high speed data detector rapid. The image resolution was 512×512 pixels (pixel size 0.4 mm). The sample to detector distance was 3.5 m. Collection time for each pattern was 10 s.

The rheometer to generate the shear flow field is a homemade parallel plate system described elsewhere [14]. In each experiment, the polymer sample, in the form of a disc of the mentioned specific dimensions to fit in the rheometer gap, was mounted between the two mica windows of the cell. The sample was held at $T = 163$ °C, above the calorimetric melting temperature of the polymer ($T_m = 155$ °C) for 5 min. After this period, the shear deformation was applied. The shear rate was 20/s for 6 s. The same shear program was applied to a range of samples using different DBS content. After cessation of the flow field, the sample was cooled down at a constant rate of 20 °C/min. SAXS patterns were collected continuously as a function of temperature.

3. Results

The crystallization of iPP sheared melts modified with DBS was followed in real time as a function of the temperature, from the molten state ($T = 163$ °C) to room temperature by SAXS. In Fig. 1 the two dimensional SAXS patterns from the sample iPP1, obtained at selected temperatures, are presented. The pattern for the sheared melt consists mainly of an equatorial intense streak ($T = 163$ °C). This streak indicates the presence of highly anisotropic scatterers in the melt and it can be attributed to the presence of DBS fibrils oriented parallel to the flow direction [12]. As the temperature decreases, intense scattering along the meridian starts to appear ($T = 147$ °C). For lower temperatures ($T = 143$ °C), this meridional feature develops into a maximum superimposed to the equatorial streak. The maximum moves towards higher scattering angles as the temperature is further decreased ($T = 135$ °C). Finally, the maximum broadens and a less anisotropic contribution appears in the lower temperature patterns ($T = 102$ °C).

To emphasize the changes observed in the SAXS patterns with temperature, Fig. 2 shows the variation with temperature of meridional and equatorial intensity cuts for the same sample as Fig. 1. As one may observe in Fig. 2, very little changes are observed in the equatorial intensity as the temperature decreases. However, there is a strong increase in the meridional intensity as the temperatures drops below 150 °C, which finally develops into a maximum. The intensity of this maximum decreases with temperature, and the peak becomes broader. Its q position ($q = (4\pi/\lambda)\sin\theta$ where 2θ is the scattering angle) moves to higher values when the temperature decreases. The presence of this maximum in the meridional small angle scattering indicates the presence of a layered structure aligned perpendicular to the flow direction.

Application to the Bragg's law (Eq. (1)) to the position of the discrete meridional maximum allows the calculation of the long spacing (L_b) of the layered arrangements.

$$L_b = \frac{2\pi}{q_{\max}} \tag{1}$$

The meridional L_b has been represented in Fig. 3 as a function of temperature for all the samples studied here. For the unmodified sample (iPP0), L_b decreases slightly as the sample is cooled, whereas samples containing DBS exhibit a stronger L_b dependence with the decreasing temperature. Also is worth mentioning that, for iPP0 and the sample with the lower DBS content (iPP0.3), L_b cannot be detected until the temperature is lower than 120 °C. The final L_b values obtained at low temperatures (measured at 50 °C), when the samples do not further crystallize, depend on the DBS concentration, (Fig. 3), varying from 160 Å in the case of iPP0 to approximately 200 Å for the samples with DBS content above 0.5%.

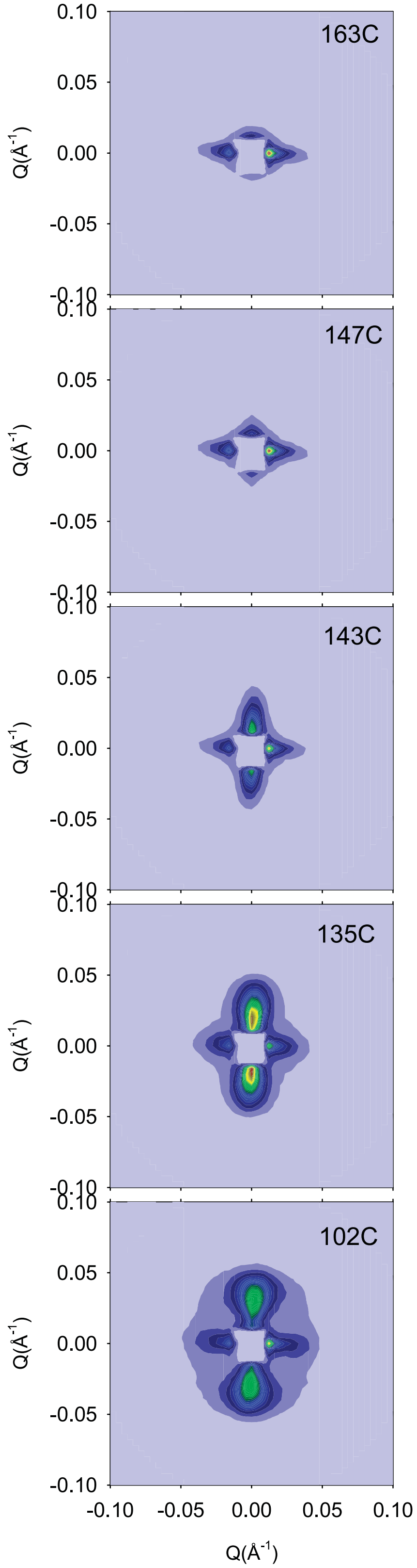

Fig. 1. Selected two-dimensional SAXS patterns obtained during cooling after the cessation of the shear flow.

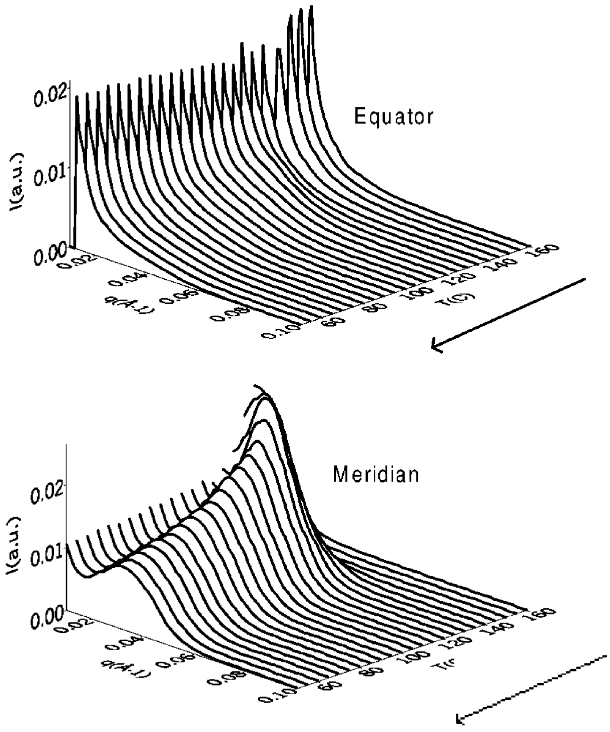

Fig. 2. Scattered intensity in the equatorial (top) and meridional (bottom) direction as a function of the scattering vector q, for different temperatures.

The total scattered intensity ($I_{\rm tot}$) in the SAXS patterns is due to the contribution of the different scatterers in the sample. On one hand, the equatorial streak in the modified melt samples is due to the DBS fibrils [12] that, as mentioned above, are oriented parallel to the flow direction. On the other hand, as the temperature is lowered, the appearance of polymer crystals aligned perpendicular to these fibrils, contributes to the total scattered intensity with an increase in meridional region of the SAXS patterns. The temperature evolution of the total scattering ($I_{\rm tot}$) is presented in Fig. 4. For all the studied samples the variation of $I_{\rm tot}$ with temperature exhibits a similar trend. As the

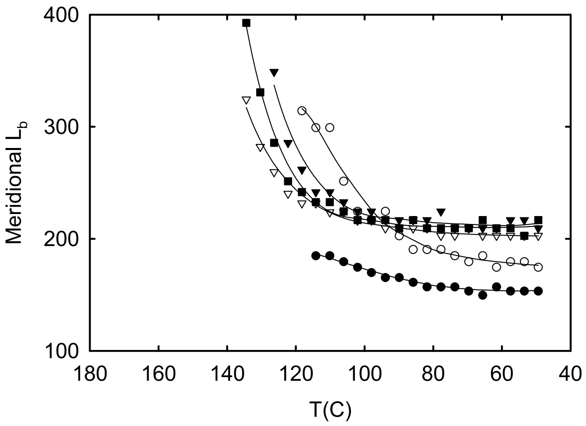

Fig. 3. Meridional long spacing (L_b) as a function of temperature for samples with different DBS concentration (●) iPP0, (○) iPP0.3, (▼) iPP0.5, (▽) iPP1, (■) iPP20. Lines are just eye guides.

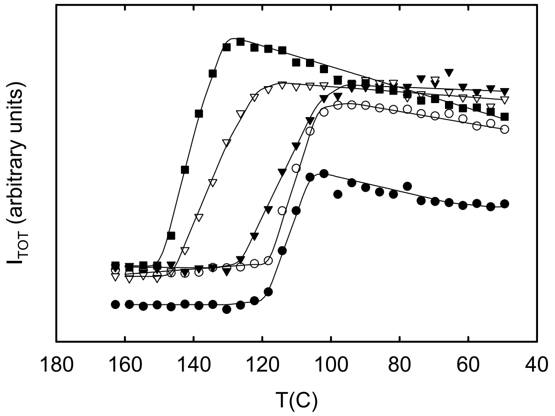

Fig. 4. Total SAXS intensity (I_{tot}) as a function of temperature for the samples studied in this work. (●) iPP0, (○) iPP0.3, (▼) iPP0.5, (▽) iPP1, (■) iPP20. Lines are just eye guides.

sample is cooled, I_{tot} presents a plateau for a temperature range, followed by a rapid increase and, after reaching a maximum, a slight decrease. The fact that, in the initial temperature range, I_{tot} does not increase suggests that, in this temperature region there are not more scatterers than those present in the melt (i.e. the DBS fibrils). The rapid increase may be associated to the development of polymer crystals. The final slow decreases of I_{tot} with temperature may be associated with further crystallization, that fills in the existing gaps, producing a decrease of electron density contrast.

In order to estimate the amount of anisotropic growing crystals from the SAXS patterns the total intensity was separated into two components: an isotropic component arising from the randomly distributed scatterers on the sample, and an anisotropic component, due to the presence of oriented species [3,7]. The total intensity is therefore represented as:

$$I_{\mathrm{total}} = I_{\mathrm{iso}} + I_{\mathrm{or}} \tag{2}$$

The isotropic component is azimuthally independent (I_{iso}) whereas the anisotropic contribution exhibits dependence with the azimuthal angle (I_{or}). Such an approach implies that I_{iso} arises only from randomly distributed objects, whereas every oriented scatterer in the sample will contribute to the total intensity only with an anisotropic intensity.

In the case of the SAXS patterns obtained here, the anisotropic intensity is arising from two different kinds of oriented specimens. On one hand, the equatorial intensity is due to the presence DBS fibrils oriented parallel to the flow direction (I_{DBS}). This intensity is approximately constant during the crystallization process. On the other hand, the lamellar polymer crystals that grow perpendicular to the flow direction produced a meridional scattered intensity ($I_{\mathrm{or.cryst}}$). Therefore, to estimate the fraction of oriented polymer crystals, one should consider only the contribution from them to the total oriented scattering, and to the total scattering. Assuming that the intensity from the DBS does not change with the crystallization process, one estimation for I_{DBS} arises from the oriented intensity obtained at high temperatures, above the crystallization temperature of the polymer ($I_{\mathrm{or}(T=160\,^{\circ}\mathrm{C})}$). The fraction of oriented polymer crystals ($\Phi_{\mathrm{or}}^{\mathrm{cryst}}$) can be obtained from Eq. (2), by:

$$\Phi_{\mathrm{or}}^{\mathrm{cryst}} = \frac{(I_{\mathrm{or}} - I_{\mathrm{DBS}})}{(I_{\mathrm{total}} - I_{\mathrm{DBS}})} \tag{3}$$

$\Phi_{\mathrm{or}}^{\mathrm{cryst}}$, estimated according to Eq. (3), has been presented in Fig. 5 as a function of temperature for all the samples studied. For iPP0 $\Phi_{\mathrm{or}}^{\mathrm{cryst}}$ remains negligible during the experiment. According to the long spacing data shown in Fig. 3, the sample exhibits a clear lamellar structure for temperatures below $T=120\,^{\circ}\mathrm{C}$. However, crystallizing the unmodified sheared melt produces randomly distributed crystals. The iPP0.3 sample exhibits a finite but rather low oriented fraction in the melt ($T=163\,^{\circ}\mathrm{C}$) and it remains nearly constant during the crystallization process. For samples iPP0.5, iPP1 and iPP20 the sheared melt exhibits a degree of anisotropy. As the temperature decreases, there is a jump in $\Phi_{\mathrm{or}}^{\mathrm{cryst}}$ to a value of about 0.6 and a subsequent slight decrease for these samples.

4. Discussion

4.1. Onset of crystallization

In the experiments presented above, the changes induced by the presence of different amounts of DBS in the crystallization behaviour of iPP are highlighted. The total scattered intensity, I_{tot}, is related to the amount of scatterers in the material. In the melt, the presence of scattering preferentially along the equator is related to the existence of DBS fibrils with a particular orientation. As the temperature decreases, the formation of crystalline lamella contributes to I_{tot}. Therefore, the total intensity is a combination of DBS

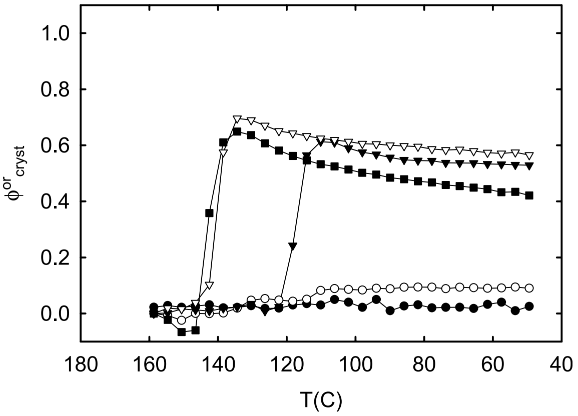

Fig. 5. Oriented fraction of polymer crystals ($\Phi_{\mathrm{cryst}}^{\mathrm{or}}$) obtained from SAXS for all samples studied as a function of temperature. (●) iPP0, (○) iPP0.3, (▼) iPP0.5, (▽) iPP1, (■) iPP20. Lines are just eye guides.

fibrillar arrangements, lamellar population and orientation and density contrast between the different phases in the system. The high impact of DBS in the crystallization behaviour of iPP can be inferred from Fig. 4. We shall consider first the temperature at which I_{tot} increases drastically, and that, as mentioned above, is a signature of the onset of crystallization. This onset exhibit clear dependence with the DBS content. In Fig. 4 it is observed that for iPP0 and iPP03 the crystallization onset is very similar whereas for higher DBS concentrations, the development of polymer crystals is shifted towards higher temperatures. It is worth pointing out the case of the highest DBS content (sample iPP20) where the onset of crystallization is detected for temperatures as high as 150 °C, which is 30 °C above the onset of crystallization for iPP0. Recent experiments on a similar iPP systems show that the addition of DBS (about 0.5% in weight) [16] increases the nucleation density for a particular temperature, on around five orders of magnitude when compared to the unmodified material and that, in the case of the sample with some DBS content, the temperature dependence of the nucleation density in this case decreases only slightly with temperature [17]. The enhancement in crystallization at higher temperatures, observed in Fig. 4 is hence due to the amount of DBS fibrils, and probably to the size of them. DBS is widely used in polypropylene manufacturing as a clarifying agent. It is often assumed that the clarifying effect is directly related to the nucleation ability. The presence of DBS fibrils provides surfaces for nucleation. In this case, for low DBS content, the addition of low amounts of DBS produces optically clearer samples [10]. However, as derived from our results, at a given temperature, increasing the DBS content increases the nucleation ability, although the optical haze is also increased, due probably, to the size of the DBS aggregates. Previous investigation also point out that the nucleation ability of DBS reaches a maximum for very low concentrations (as low as 0.5% in weight) [9]. However, the present results show that this is not the case, and that if there is any saturation, it occurs at much higher concentrations, certainly higher than 1%, as evidenced by the differences in the onset of crystallization displayed by iPP1 and iPP20.

4.2. Development of highly aligned structure

As it is discussed elsewhere [12], the melt SAXS pattern shown in Fig. 1 ($T=163$ °C) for the DBS modified PP melt can be explained by considering the presence of a DBS fibrillar structure dispersed in the polymer melt. The shear field produces a preferential alignment of the fibrils parallel to the direction of the flow [12] and therefore a very intense scattering is observed in the equatorial direction. The development of meridional reflections can be associated with the formation of a periodic arrangement of crystalline lamella oriented perpendicular to the previously applied flow fields, and therefore, perpendicular to the DBS fibrils. The presence of highly anisotropic crystals is directly ascribed to the presence of DBS fibrils. Moreover, it is due to the presence of a sufficient amount of DBS fibrils. Samples with none or very little amount of DBS, do not exhibit polymer crystalline orientation after crystallizing the sheared melts. However, for a critical DBS concentration (between 0.3 and 0.5% in weight according to the present results) the orientation induced to the fibrils by the deformation in the melt it is templated into the polymer crystals.

As explained in the previous section, the temperature at which the crystallization occurs is related to the DBS content. Low DBS amounts do not produce any increase in crystallization temperature compare to the pure polymer (Fig. 4). In samples with high concentrations of DBS, $\Phi^{\mathrm{or}}_{\mathrm{cryst}}$ increases dramatically coinciding with the onset of crystallization. That means that the first crystals to grow are almost perfectly aligned perpendicular to the DBS fibrils. The long spacing of the crystallized samples (i.e. measured at $T=50$ °C), obtained from the SAXS patterns, exhibits a clear dependence with the DBS concentration. As discussed by White and Basset [18] these differences cannot be attributed solely to different nucleation geometry. Also, they cannot be attributed to the shearing conditions, since all samples, regardless of the DBS concentration where processed under the same conditions. The explanation may be inferred by comparing Figs. 3 and 4. In the samples with higher amounts of DBS the crystallization starts, upon cooling, at higher temperatures, leading consequently, to thicker polymer crystals. On top of that, the peculiarities of the α form of iPP may induce these observed high values of L_{b}. Typically, the α form of iPP consist of a crosshatched structure of parent and daughter lamellae, where the secondary or daughter lamellae nucleate and grow from previously formed primary lamellae (the parents) [19].

Also, as reported in the literature [18], crystallization of iPP at higher temperatures produces a lower amount of secondary lamellae, which are thinner than the primary one. This effect, together with the crystallization at higher temperatures will account for the observed higher L_{b} obtained for samples with high DBS concentration.

It is interesting to quote here the case of the iPP03 sample, where, only a little amount of orientation is developed in the melt, and also very slight orientation of the polymer crystals is observed. The fact that DBS builds a network of fibrils within the polymer melts may explain this situation. Here we hypothesize that, in the system we are dealing with, the network created by DBS when dispersed in very low quantities (0.3% in weight in this particular case) is very loose, and therefore, it does not respond to the deformation with a clear alignment. Also, since the network is very loose, the DBS fibrils will be far away one from another. Therefore, the lamella growing in direct contact to the DBS surfaces will be oriented. But this orientation will be diffused as the lamellae grow outwards.

From the results presented here it is possible to conclude that the oriented DBS fibrils in the melt, in amounts above a certain threshold, are able to nucleate iPP crystals in a wide range of temperatures. The alignment of these fibrils in the polymer melt is responsible for templating and enhancing the polymer crystal orientation.

5. Conclusions

The presence of DBS in the form of fibrils nucleates the polypropylene crystals in a wide range of temperature, dependent on the amount of DBS present in the system. The fibrils are aligned parallel to the flow direction.

The SAXS patterns of the DBS nucleated systems crystallized from sheared melts reveal the presence of high levels of crystalline orientation, oriented perpendicular to the shear flow, and hence, perpendicular to the DBS fibrils.

The initial crystals exhibit a high degree of orientation. As the crystallization process continues, the growing crystals are distributed more randomly, as revealed by the decrease in the oriented fraction.

The DBS fibrils enhance the crystallization at higher temperatures than in the pure iPP. The long spacing arising from the lamella stacks in the DBS modified polymer is higher, indicating that the formed crystals are thicker.

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