



OPTICAL ANALYSIS OF ISOTACTIC POLYPROPYLENE: CHARACTERIZE THE TYPES OF ISOTACTIC POLYPROPYLENE SPHERULITES α AND β , AND THEIR OPTICAL PROPERTIES

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ABSTRACT

The optical properties of isotactic polypropylene were studied according to different crystallization temperatures. Early beginning of growth of isotactic polypropylene were observed at different stages of growth, where the structures begins with primary nuclei developed through isolated single lamella, then develops into a lamellar sheaves and finally attains the spherulitic structure. Two main types of spherulites, α and β spherulites appears for the isotactic polypropylene over a wide range of crystallization temperature. However, the difference between spherulites types appears due to the difference in its contents of radial lamellae and cross hatching beside the difference in crystallization temperature and melting points.

Keywords: Isotactic polypropylene, fiber morphology crystallization, spherulites, optical properties.

INTRODUCTION

Polypropylene is one of very important polymers, it has double forms; plastic and fiber. Isotactic polypropylene is known to exhibit in several crystalline forms, the monoclinic α -form, the hexagonal β -form, and the triclinic γ -form (Norton and Keller, 1985; Varga, 1992). While, α -form is the stable and is also the most prevalent one. The β -form is observed occasionally during crystallization and it appears as a minority constituent of the isotactic polypropylene. Under special crystallization conditions or when selective β -nucleates are used, higher levels of the β -form can be produced (Tjong *et al.*, 1996). The microstructures and mechanical properties of α -form isotactic polypropylene have been investigated extensively. In contrast, fewer studies have been made on the morphology and mechanical behavior of the β -form isotactic polypropylene. Another study, Jeffery *et al.* (2000) have reported different levels of the β -form by adding a small amount of a quinacridone dye nucleation agent. They also reported that isotactic polypropylene which contains high levels of the β -form exhibits lower values of the modulus and yield stress but higher elongation at break. Pawel (1994) investigated that a high purity of the β -phase can be formed in isotactic polypropylene by adding a specific biocomponent β -nucleator consisting of equal amounts of pimelic acid and

calcium stearate. The relative β -phase content can reach as high as 94% by adding only 0.001 of such β -nucleates. Clark and Hoffman, (1984) studies the existence of two crystal growth regimes. The occurrence of a regime III/II transition would exhibit a downward change in the slope with increasing crystallization temperature. The regime III to regime II transition occurred near 137°C. Earlier study, Allen and Mandelkern (1987) reported a regime II/I transition at about 152°C. They found that the regimes do not serve as boundaries between distinct morphological textures. Sadler (1987) found that low molecular mass ipp fractions, the presence of a regime II/I transition is well-defined by both observations from linear crystal growth and overall crystallization measurements. Data from morphological observations carried out from solutions and from the melt (Khoury, 1966) show a three dimensional array of a nearly orthogonal cross-hatched lamellar texture. Solution crystallization studies have elucidated the basic morphology as being lath line chain-folded lamellar crystals. These crystals formed relatively open networks in solution –grown aggregates, while tightly interwoven textures appeared during melt crystallization. It has been observed that such lamellar branching is characterized by the constant angle between daughter and mother lamellae (80° or 100°). From the two orthogonal components of the cross-hatch, the radial lamellae (mother lamellae) by themselves would generate negatively birefringent spherulites as in β -form spherulites. The tangential lamellae (daughter lamellae)

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would generate their own positive birefringence. However, the latter occurs in combination with the radial lamellae. The presence of the tangential lamellae reduces the negative birefringence and if in sufficient quantity, may actually impart their own sign, rendering the spherulite positively birefringent. From the previous studies, there appears to be no morphological distinct stage where birefringence changes from positive to negative during isothermal crystallization or heating. In this work, particular attention is served to crystallization conditions and their influences on the melting behavior and morphological change in the isotactic polypropylene. Van der Meer (2003) found that the isotactic polypropylenes synthesized by metallocene catalysts show unique properties in the sense that the system allows us to study the influence of two different kinds of defects on the crystallization.

In this study we want to characterize the types of isotactic polypropylene spherulites α and β , and their optical properties.

MATERIALS AND METHODS

During this study the used materials are a homopolymer of isotactic polypropylene originally supplied by (PSCC) at RAPRA, SHAWBURY, SHOPSHIRE, UK. Its molecular mass has been measured by PSCC to be $M_n=4.7 \times 10^4$ and $M_w=4.2 \times 10^5$. The samples were used in the pellets form.

Optical Microscopy

In the present study, the sample was placed on a Nikon microscope type (FX-35DX) with cross polarization condition. The sample is in the hot stage above the melting point of ipp at 200°C , and then it was cooled to different crystallization temperatures. The spherulitic growth at crystallization temperature was monitored in most cases and the resulting spherulites were photographed by Nikon 35 mm, the Nikon microscope was connected to photo monitor to measure the transmitted light intensity of spherulites.

RESULTS AND DISCUSSION

In our study for the α -phase the melting is associated with a continuous decrease of the relative light intensity until 145°C , above that temperature there is an increase in the relative light intensity associated due to the melting and recrystallizing of the cross-hatched lamellae which are thin to form more radial perfect lamellae, at crystallization temperature 140°C the form α - spherulites has mixed from α_1 and α_2 -spherulites, so that there is a slight increase in the light intensity which is transmitted from the mixed α - spherulites (Zhang *et al.*, 1996).

As we see that the scanning electron micrograph given in Figure 1, shows embryos appearing as 100 nm dots in many regions as shown in the optical micrograph of isotactic polypropylene crystallized from the melt, after several minutes from the isothermal crystallization at 125°C . The observations demonstrate that an embryo below a critical size disintegrates. The embryos can be seen in the regions A and B. In Figure 2. These embryos have growing fronts where polymer chain segments fold into the crystal lattice. Eventually, similar embryo grows into a founding lamella as shown in region A Figure 3.

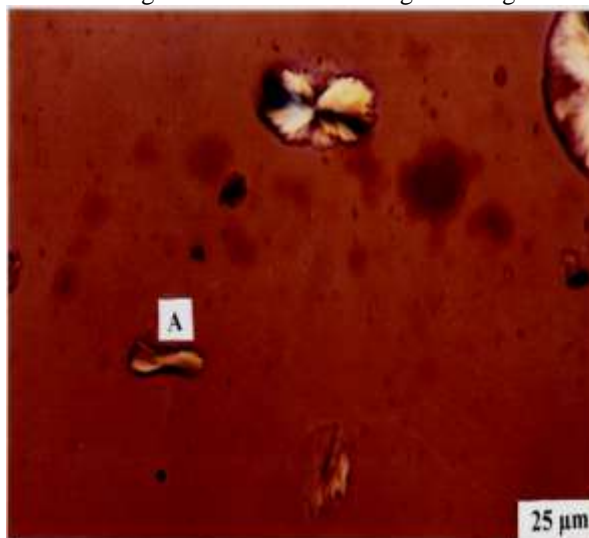


Fig. 1. Optical photograph of isotactic polypropylene crystallized from the melt at 125°C , under crossed polarization conditions showing the beginning of embryos appearance as a dots in many places in addition to other objects as growing lamellae as shown in region A.

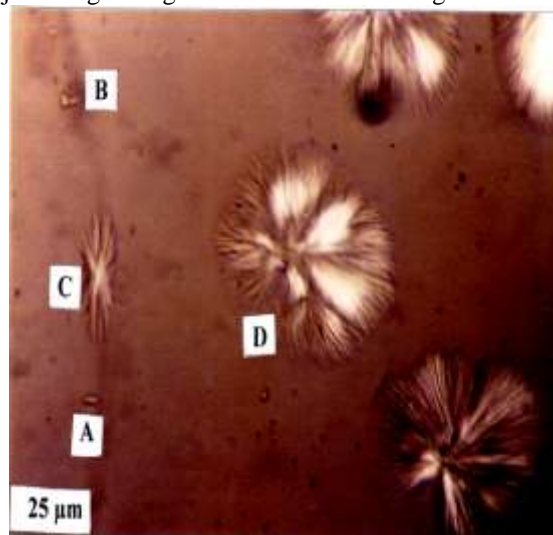


Fig. 2. Optical photograph of dots embryos of isotactic polypropylene in different places in addition to isolated lamellae as shown in region A and B. the figure shows also more advanced growing objects such as the multilayer branching region C and sheaf-like object region D. the crystallization temperature is 125°C .

Another embryo can be found in the middle of Figure 4, this embryo appears to integrate to form an isolated single lamella. An embryo below a critical size is not stable, so that it can disintegrate. Once an embryo grows larger than the critical size, as predicated by the thermodynamics keynities, it can grow continuously at both ends and develop into a single lamella as shown in Figure 3 region A.

There is a founding lamella in Figure 1 region A. this founding lamella grows in two directions. Branching occurs in the middle of founding lamella, so that an induced nucleus formed next to the founding lamella, developed into a subsidiary lamella.

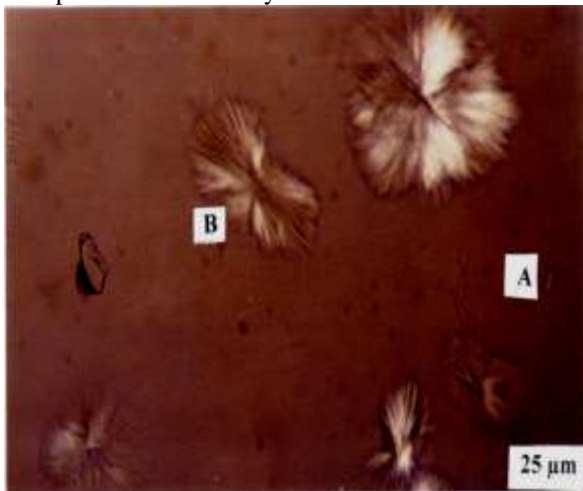


Fig. 3. Optical photograph of isotactic polypropylene, crystallized at $T = 125^{\circ}\text{C}$. showing isolated single lamellae region A and different orientation of the a sheaf-like object region B.



Fig. 4. Optical photograph of isolated single lamella of isotactic polypropylene which crystallized at $T_c = 125^{\circ}\text{C}$.

Such subsidiary lamella then grows both forward and backward. Therefore, other subsidiary lamella is formed at both sides of the founding lamella as shown in region C

Figure 2. Branching and splaying continue, so that, as can be seen for similar founding lamella, the structure develops into a lamellar sheaf consisting of many lamella as shown in region B Figure 3. High degraded isotactic polypropylene can be produced when the sample of iPP crystallized from melt has low thickness, as shown in Figure 5 highly degraded sample shows positive α -spherulites independently of the crystallization temperature, where monofibrils and small angle branches of fibrils became visible even by optical microscopy.

At the edges of the specimen where it's crystallized from the melt, there is a lack of crystallization of isotactic polypropylene. This can be seen in Figure 6. In this figure the sample was crystallized isothermally at 145°C , where it can be seen to be a composite structure of narrow central thread strung with small platelets. This behavior is similar to the narrow fibrils which become overgrown with platelets in the characteristic fashion when they are allowed to nucleate from polymer solution (Al-Raheil *et al.*, 1998a). In short, this fiber morphology is regarded as it clearly obvious, as a nucleation of fibril followed by epitaxial overgrowth of lamellae sharing a common chain axis orientation along the fiber. The fiber itself results from strain-induced crystallization, which means that, from distorted molecular conformations in which chains have been brought and maintained parallel for long enough to nucleate crystallites. The circumstances where such fiber to occur, is probably involvement of some stresses on partly melted molecules as the growth moves through the melted polymers in convective flow. The fiber growth in the molten polymer has a great technical importance, being related to processes of molding and extrusion.

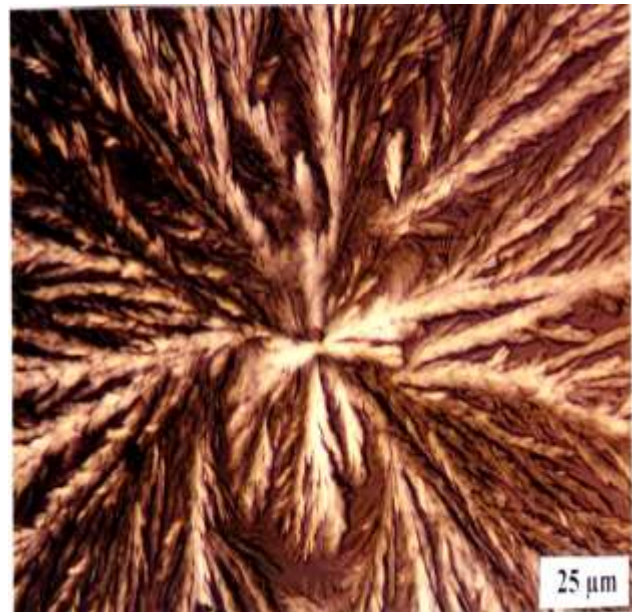


Fig. 5. Optical photograph of highly degraded α -spherulites, $T_c = 135^{\circ}\text{C}$.

It is now possible a more informed look at row nucleation in crystallization of isotactic polypropylene from the melt as exemplified by Figure 7. When the melt is under strain the probability of bringing chains parallel for long enough to nucleate a crystal embryo will increase.

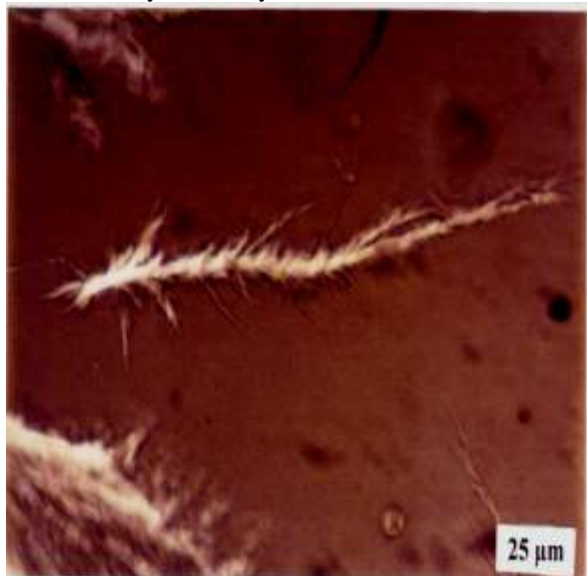


Fig. 6. Optical photograph of fiber morphology crystallization of isotactic polypropylene at the edge of specimen, $T_c=145^\circ\text{C}$.

As it does for fiber morphology, once a crystallite has formed, the chance of generating a row nucleus in this way will increase with strain and with crystallization temperature. After a row nucleus has formed it is likely to initiate transverse growth perpendicular to the direction of strain. The reason for this row nucleation is that molecular conformations are being drawn out, the more so far longer molecules. Moreover, the extension in the flow field will tend to form a series of nuclei in a row positively discourage molecular back folding. One expects therefore, row nuclei containing reasonably chain-extended molecules on which may deposits, under suitable conditions of low temperatures and modified flow, lamellar overgrowths.

Figure 8 shows an intermediate stage of growth in a different part of specimen for isotactic polypropylene crystallized from melt at 125°C . This figure shows two kinds of spherulites, the first is α -type spherulites and exhibits a dark contrast, the second is a β -spherulites having a bright contrast. In all observations which were carried out on the crystallization of this polymer at 125°C , the measurements indicates that the growth of β -type spherulites is slower than α -type spherulites, with an agreement with the results obtained previously by Al-Raheil *at el.* (1998b), where they found that β -type spherulites appear to be slower in growth than α -type spherulites up to 142°C , and above 142°C the α -type spherulites has higher growth due to low temperature

melting of β -spherulites. They found also the β -spherulites usually form only when the crystallization temperature is below 132°C . To measure the growth rate of β -spherulites above 132°C the procedure is to make two step crystallization. The first step is to crystallize the specimen of isotactic polypropylene at temperature below 132°C . Once the β -spherulites appear in the specimen at the early stages of growth, the temperature of the specimen can be raised to higher crystallization temperature more than 132°C ; therefore the growth of β -spherulites can be measured at the new temperature, as a second step of crystallization.

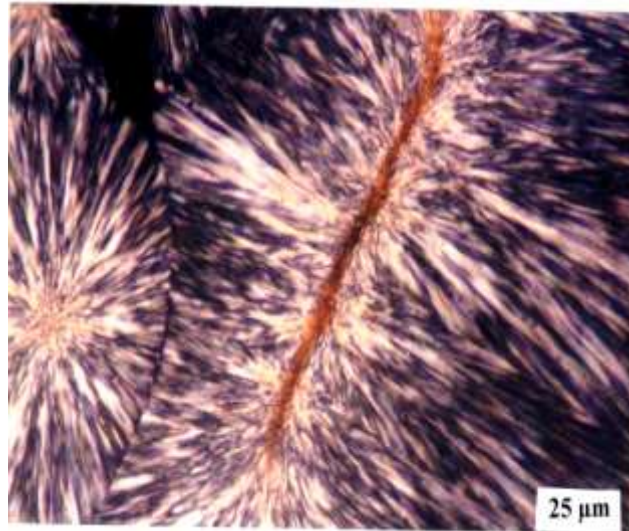


Fig. 7. Optical photograph of row nucleation in crystallization of polypropylene which crystallized at $T_c=128^\circ\text{C}$.

However, it was found in the present results, the proportions of β -spherulites are much less than α -spherulites for samples which contain both modifications, the proportions of β -type spherulites decreases with increasing the crystallization temperature, and it cease, completely to be appeared above 132°C crystallization temperature, if the crystallization was carried by one step above the mentioned temperature. However in most cases, the β -form does not exceed 15% of the crystallization material. Figure 9 shows a region of isothermally crystallized sample of 128°C . In this figure two modification of α and β spherulites can be identified. In general, the β -spherulites have a larger size than α -spherulites, despite the fact that β -phase occupies, on the whole, a smaller fraction. It can be seen that interspherulitic boundary between boundary the α and β -types is always curved, with the concavity oriented towards the α -phase. The reason for the concavity is due to the higher crystallization growth of β -spherulites at that temperature. Upon heating, the β -phase melts at 152°C leaving the α -spherulites alone as shown in Figure 9 and 10. The contrast of α -type spherulites can be seen in Figure 9 as dark region with positive birefringence due to high

density of cross-hatching lamellae. The α -spherulite in Figure 9 can be identified as α_1 -type. With increasing the temperature, the cross-hatching lamellae start to melt gradually. Therefore, the dark contrast of α_1 -type spherulite changes to bright with negative birefringence due to the melting of tangential lamellae as shown in Figure 10. According to that there is a transformation from type α_1 to α_2 spherulites, and the α -spherulites which can be seen after melting of β -spherulites in Figure 10 can be considered as α_2 -type. In fact, the two types of α -spherulites (Padden and Keith, 1959) are distinguishable by the different degrees of cross-hatching. Hence, without the cross-hatched lamellae, the spherulite should be a type α_2 .

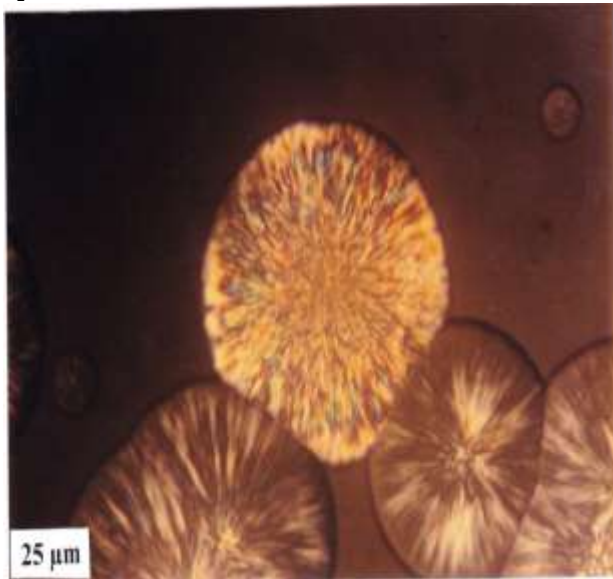


Fig. 8. Optical photograph of two types of spherulites α -spherulites and β -type spherulites, the β -spherulites is bright while the α -spherulites have a dark appearance, $T_c=125^\circ\text{C}$.

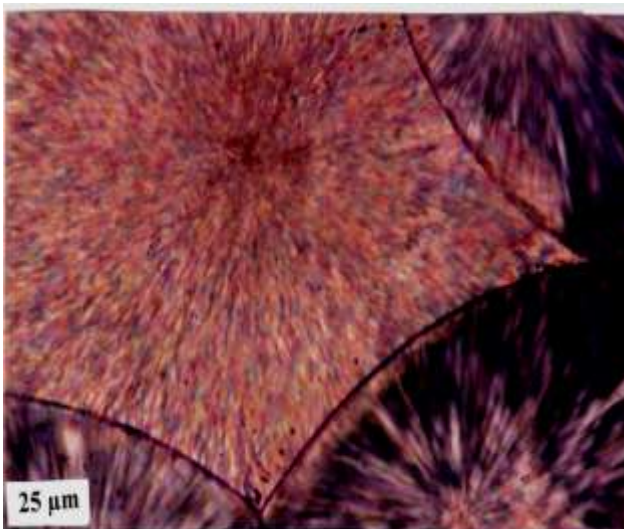


Fig. 9. Optical photograph of α -spherulites and β -spherulites, $T_c=128^\circ\text{C}$.

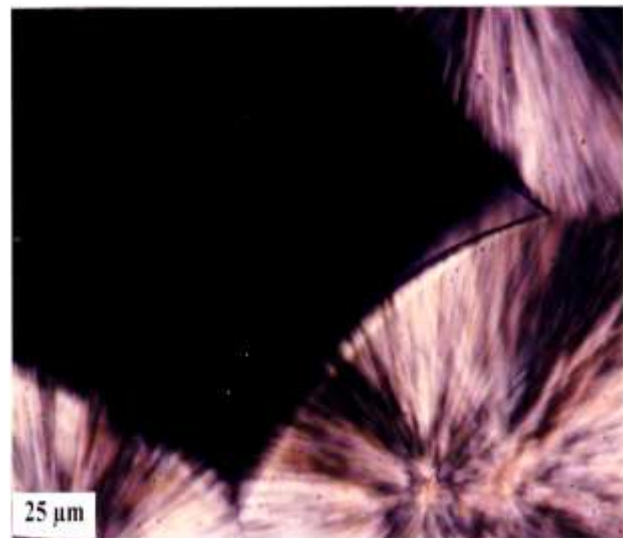


Fig. 10. Optical photograph of melting of β -spherulites at $T_m=152^\circ\text{C}$, $T_c=128^\circ\text{C}$.

CONCLUSION

According to the above results, it's clear that the isotactic polypropylene is crystallized from melt. Four types of spherulites were identified; β -spherulite, α_1 -spherulites, α_2 -spherulites and mixed α -spherulite. β -spherulites and α_1 -spherulites form below 132°C , mixed α -spherulites grows in temperature range 132 - 145°C , while α_2 -spherulite forms at high crystallization temperature above 145°C . α_1 -spherulites contains two types of lamellae cross-hatch and radial lamellae, but α_2 -spherulites contains only the radial lamellae, so that the mixed α -spherulites has lower contents of cross-hatch lamellae comparing with pure α_1 -spherulite. For sample contains two modifications of α and β -spherulites, it was observed that β -spherulites melts first at 152°C while α -spherulites melts at 167°C . Sometimes if there are induced strains in the melt crystallized isotactic polypropylene fibril structures and row nucleation may be observed.

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