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The structure of Isotactic Polypropylene Crystallized from the Melt

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Abstract

The melting behavior of isotactic polypropylene was studied in the hot stage mounted on polarizing optical microscope supported by photomonitor. Over a wide range of crystallization temperature there are two main types of spherulites, α and β spherulites for this polymer α spherulites may exist in three forms α_1, α_2 and mixed of α_1 and α_2. The α_2-form can be obtained at high crystallization temperature above 145°C and α_1 can be observed at low crystallization temperatures below 132°C. The mixed α-spherulites can be obtained between 132°C and 145°C. However, the β-phase form small proportion of the total phase not more than 15% and usually exist when the crystallization temperature below 132°C. If the sample crystallized from the melt it shows usually two melting peaks. However, when the temperature of the sample was increased to crystallize in a second step at higher temperature it shows two melting peaks and if the second step of crystallization was very close to melting point it shows only one single peak, since the reorganization of crystals process will be stopped completely.

Keywords: Isotactic polypropylene; Crystallization; Spherulites; Melting point

Introduction

Spherulites develop from crystallites starting from a central nucleus and growing in all directions radially, with small angle of branching in between. The branching provides space filling. The first theory about crystallization in polymers was founded by Padden and Keith [1] and later according to the phenomenological observations that theory was crystallized by Bassett and Vaughan [2]. They found that the small angle fibrillar branching is induced by impurities has low tendency to crystallize and, therefore, segregation will be found in the vicinity of growing front.

According, to Varga revision [3] when isotactic polypropylene is crystallized from the melt, is monitored by polarizing optical microscope, birefrengent spherulites are produced, growing radially at a constant rate under isothermal conditions. Due to impingement of growing spherulitic fronts, the structure formed will consist of polygonal formations confined by straight or curved lines after complete crystallization.

During the crystallization of isotactic polypropylene, Varga [4] found that, two types of spherulites α-and β-modification. Under given thermal conditions the two types develop simultaneously.

Padden and Keith [5] found that three types of α-spherulites might be formed depending on crystallization conditions: positive radial below 133ºC, negative radial above with no cross-hatching lamellae above 137ºC and a mixed type in between.

In this paper non-isothermal crystallization melt behavior and thermal properties of isotactic polypropylene, ipp, were studied with respect to different crystallization temperatures from the molten state to see the effects on the crystallization behavior and spherulitic structure.

Experimentals

Materials

The materials of this study are a homopolymer of isotactic polypropylene originally supplied by polymer supply and characterization center (PSCC) at Rapra, Shawbury, Shopshire, UK. Its molecular mass has been measured by PSCC to be $M_n=4.7\times10^4$ and $M_w=4.2\times10^5$. The samples were received in the form of pellets.

Optical microscopy

The sample was prepared by squashing ipp sample between slide and cover slip on a hot plate. Then it was inserted inside Mettler (FP82) hot stage connected with a computer reinforced with special software from Mettler Company. The hot stage was mounted on a Nikon microscope type (FX-35DX) with cross polarization condition. The sample inside the hot stage was heated above the melting point of ipp at 200°C, and then it was cooled to different crystallization temperatures below its melting point. The spherulitic growth at crystallization temperature, was monitored in most cases and the resulting spherulites were photographed by Nikon 35 mm camera type (FX-35 DX), or the Nikon microscope was connected to photo monitor to measure the transmitted light intensity of spherulites.

Thermal analysis

The melting and crystallization behavior for isotactic polypropylene samples was studied using Mettler DSC model (FP 85) connected with a computer. Each sample was carefully prepared and measured to have weight between 10-14 mg, by using microbalance with sensitivity 10 micrograms.

Isotactic polypropylene samples were placed inside aluminum crucibles, then the crucibles were heated in the DSC above the melting temperature of ipp at 200°C (the melting point is about 170°C), and the sample kept in the DSC cell for about one minute to melt most of

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crystalline nuclei. Then the sample was cooled below its melting point to the required crystallization temperature for different times. After that the samples were heated from crystallization temperature at rate 10°C.min^{-1} to 200°C. In sometimes the sample were cooled from the crystallization temperature to lower temperatures, and then heated at rate 10°C.min^{-1}.

In all measurements the melting behavior was seen in the computer screen, so that the changes of the heat flow with increasing temperature due to structural changes of the samples were recorded.

For optical studies the sample of ipp was squeezed on hot stage glass slide and cover slip and the sample was transferred to Mettler hot stage model FP 82 and crystallized from the melt after heating to 200°C for 1 minute and cooled to the required crystallization temperatures for predetermined times.

Result and Discussion

The various spherulites morphology of isotactic polypropylene was analyzed in details [6]. Two types of spherulitic microstructures are encountered in the α-form. Type α_1 spherulites which appear in the temperature lower than 134°C, exhibit an overall positive birefregrance when examined in a polarizing microscope, while the main lamellae are oriented radially, tangential lamellae appear to grow by epitaxial deposition, with a direction of growth which is inclined by approximately 81°C. These tangential lamellae are responsible for the sign of the birefringence that is observed. On the other hand, at a crystallization temperature higher than 140°C, negatively birefrengent spherulites are also identified, these type α_2-spherulites, therefore, presumed to contain only a small proportion of tangential lamellae, although the amount of transverse lamellae that is necessary to change the birefringence sign cannot be estimated easily. These are a consequence of in homogeneity of the spherulites where regions of predominantly radial lamellae, giving a negative birefringence, coexist with other regions which contain predominantly tangential lamellae which give a positive birefringence [7]. This assumption is supported by the results in this study when the specimen of isotactic polypropylene was crystallized from the melt at 128°C. 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 inter-spherulitic boundary between boundary 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. The contrast of α-type spherulites can be seen as dark region with positive birefringence due to high density of cross-hatching lamellae. The α-spherulites 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 spherulites changes to bright with negative birefringence due to the melting of tangential lamellae.

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 can be considered as α_2-type. In fact, the two types of α-spherulites [8] are distinguishable in this study by the different degrees of cross-hatching. Hence, without the cross-hatched lamellae, the spherulites should be a type α_2.

The bifurcation of α spherulites was studied by Varga. With increasing crystallization temperature, the relation between the growth rate of β spherulites to α spherulites decreased, and above certain temperature, $T_{\beta\alpha}$, the growth rate of the α-modification exceeds that of β modifications. The level of $T_{\beta\alpha}$ as was found by Varga was between 140°C-141°C. He also found above $T_{\beta\alpha}$ an α-nuclei are found on the surface of growing β spherulites, developing α spherulites is segments which finally overgrow the basic β spherulites completely.

In this study, it was found that the bifurcation of β α-spherulites was not detected. In contrast to the αβ-modification can be observed in many different part of the specimen. For example this can be observed in figure 1 for sample crystallized at 128°C, α spherulites was formed first and in its surface β spherulites was formed later. It is obvious that at 128°C crystallization temperature the growth rate of β spherulites is faster than α spherulites.

Recrystallization of β-spherulites into the α-modification during heated was studied by many authors [9-15]. Studies led to the assumption of thermodynamic instability of β-modification.

In this study it was found that melting of β-modification had a specific feature including a much more complicated process than that outlined above, namely the melting characteristics of β-pp are highly dependent on the thermal post history of the crystalline sample. In contrast to the studies in the above literature, when heating begins from the temperature of crystallization, the β-modification does not recrystallize in α-form; instead they melt separately. However, if the sample containing β-ipp is cooled quickly by immersing it in cold water, upon heating again the partial melting of β-form is accompanied by a recrystallization into α-form (βα-recrystallization) and finally, they melt in α-form. Consequently βα-recrystallization susceptility appears due to recooling.

An optical representation of the above transformation can be observed in figure 2 and 3. Figure 2 shows α and β-modifications at the same time, after isothermal crystallization at 125°C.

When the sample is quenched in cold water, upon heating the βα-recrystallization of β-spherulites transforms into α-spherulites preserving the shape character as shown in figure 3. The appearance of the tendency to βα-recrystallization of β-ipp quenched in cold water can be attributed to the formation of α-phase within the β-spherulites upon quenching, due to a secondary crystallization talking place in the cooling process. According to that, this phase acts as a α-nucleating agent during the partial melting of β-spherulites [16].

The transformation from α_1 to α_2-spherulites was confirmed from the melting process of ipp crystallized at 125°C by measuring

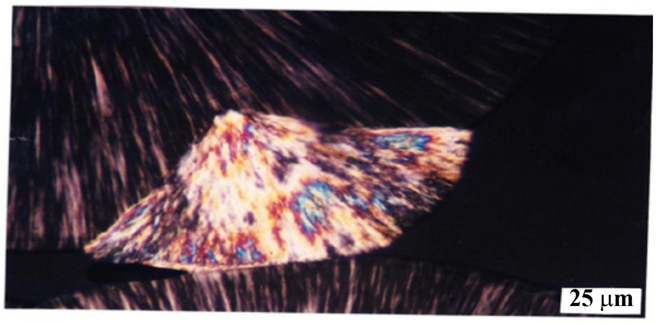

Figure 1: Optical photograph of αβ-bifurcation for sample crystallized at Tc=128°C.

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the relative light intensity of α-spherulites between crossed polarizes by applying heating rate of 10°C/min as shown in figure 4. 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 with transformation of α_1 to α_2-spherulites due to the melting and recrystallization of the cross-hatched lamellae which are thin to form radial perfect lamellae. At crystallization temperature 140°C the form α-spherulites is 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 as shown in figure 5. According to that, the transformation from mixed α-spherulites to pure α_2-spherulites is associated with a moderate increase in the light intensity, due to the low contents of cross-hatched lamellae in the mixed α-spherulites.

Pure α_2-spherulites can be obtained if the sample is crystallized in two steps. For example figure 6 shows the relative light intensity transmitted through a mixed α-spherulites grown at 140°C for 18 hours, then the sample was heated in the hot stage until 160°C for 1 hour to form the pure α_2-spherulites, then cooled again to 140°C. Upon heating there was no increase in the transmitted light intensity through the pure α_2-spherulites, at this stage it can be said that, there is no existence to the cross-hatched lamellae in pure α_2-spherulites.

Figure 7 shows the DSC endotherms traces of isotactic polypropylene, curve in figure 7 shows a board peak of endotherm of melt crystallized ipp at 125°C for 1 hour. Annealing the same sample at 155°C for 30 minutes followed by heating to 200°C as shown in curve b changes the melting trace so that there is no longer marked melting before 155°C, but at this temperature the new curve rise to accommodate with the old curve. Evidently, the crystallinity of the cross-hatched lamellae which had melted below the annealing temperature has been vanished from the spherulites structure when the sample crystallized at 125°C and annealed at 155°C.

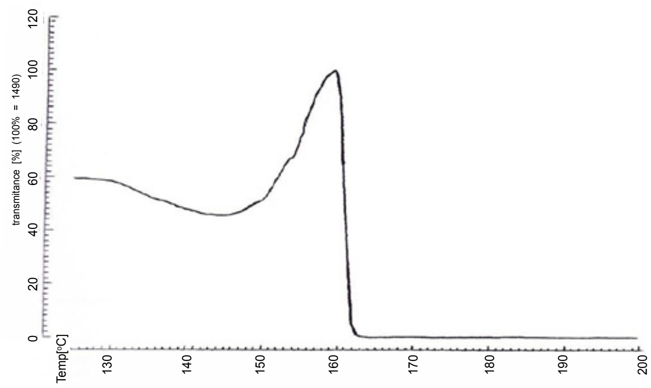

Figure 4: Transmitted light intensity of α-type spherulites of isotactic polypropylene which crystallized at 125°C for 5 hours then heated directly to 200°C at scan rate 10°Cmin^{-1}.

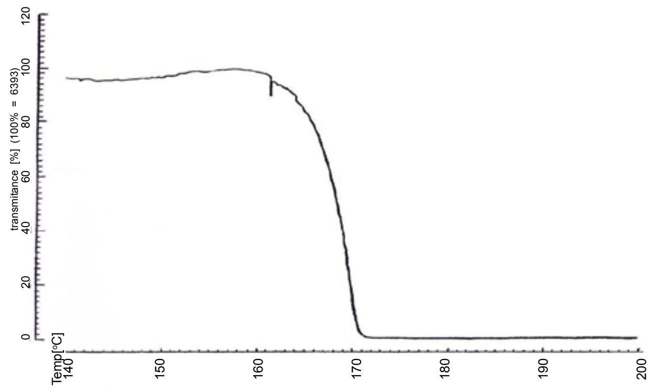

Figure 5: Transmitted light intensity of α-type spherulites of isotactic polypropylene which crystallized at 140°C for 5 days then heated directly to 200°C at scan rate 10°Cmin^{-1}

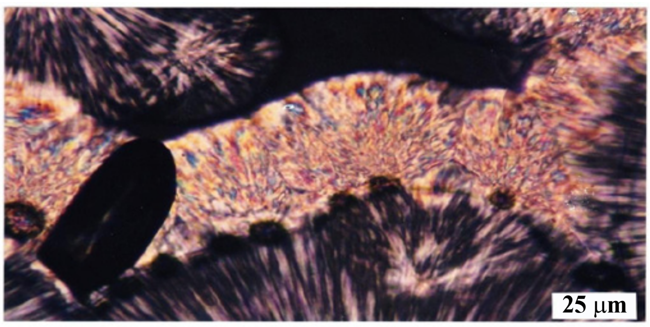

Figure 2: Optical photograph of α and β-modifications after isothermal crystallization at Tc=125°C.

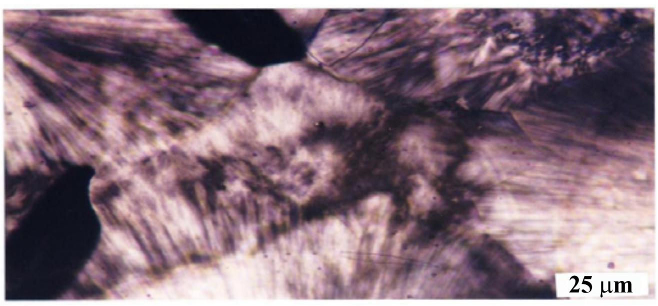

Figure 3: Optical photograph of transform of β-spherulites which are shown in figure (5), Tc=125°C.

Comparing the DSC results in figure 7 with the relative light intensity of α-spherulites for sample treated by heat in the same way as shown in figure 4, one can say that the melting behavior as shown in figure 7 belongs only to the melting of α_2-spherulites since α_1-spherulites has been transformed to α_2-spherulites at 145°C as shown from the rising in the light intensity during heating at that temperature. According to that, the melting behavior of the annealed sample at 155°C is due to the melting of the radial lamellae of α_2-spherulites.

This trend applies when the isotactic polypropylene is crystallized at 140°C for 18 hours as shown in figure 8 curve a. once the cross-hatched lamellae are melted after annealing at 155°C, curve b, the double melting behavior still exists, with no broad melting endotherm in the lower side as shown in curve a in the same figure. It is interesting to note that with no β-phase, the double melting behavior is not affected by annealing process at 155°C, therefore, the melting of cross-hatched lamellae does not belong to the lower melting peak as one can expect, it can be suggested that the melting of cross-hatched lamellae belongs only to the endotherm of the broad tail which leads the lower melting peak in curve a in both figures 7 and 8. Annealing the same sample

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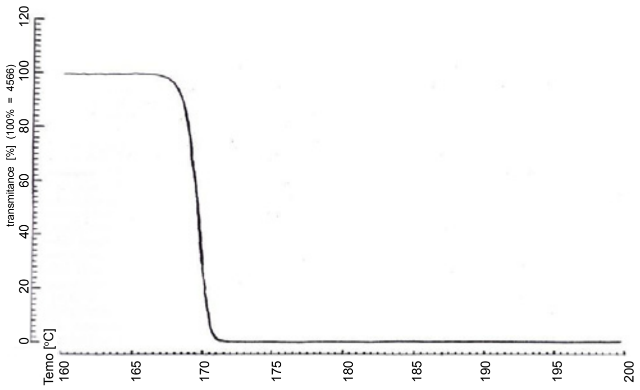

Figure 6: Transmitted light intensity of α-type spherulites of isotactic polypropylene which crystallized at 140°C for 18 hours then heated to 160°C for one hour then heated to 200°C at scan rate 10°Cmin^{-1}.

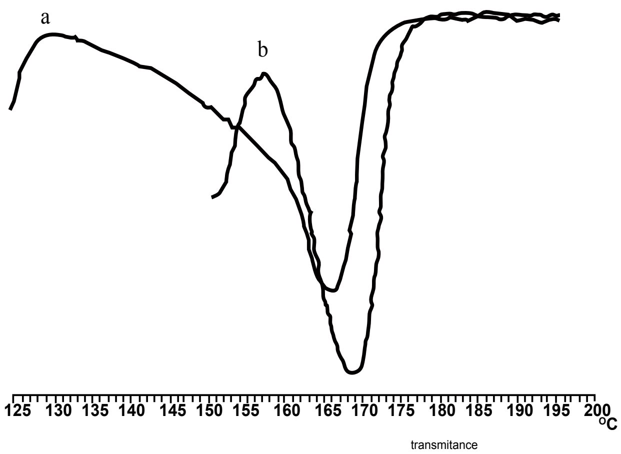

Figure 7: DSC trace for ipp isothermal crystallized from the melt at a- 125°C for one hour then heated to 200°C at scan rate 10°Cmin-1 b-125°C for one hour then annealed at 155°C for one hour then heated to 200°C at scan rate 10°Cmin^{-1}.

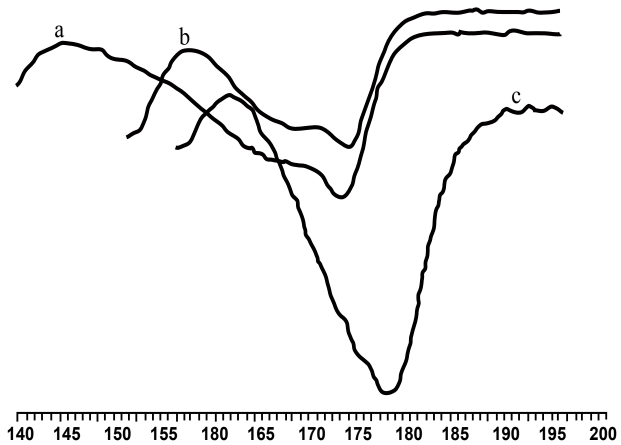

Figure 8: DSC trace for ipp isothermal crystallized from the melt at a- 140°C for 18 hours then heated directly to 200°C at scan rate 10°Cmin-1 b-Tc=140°C for 18 hours then annealed at 155°C for one 10 hour then heated to 200°C at scan rate 10°Cmin-1 c- Tc=140°C for 18 hours then annealed at 160°C for one hour then heated to 200°C at scan rate 10°Cmin^{-1}.

which has been crystallized at 140°C for 18 hours at 160°C for 1 hour then heating directly 200°C as shown in curve c figure 8, changes the double melting behavior to single melting peak. At this high annealing temperature, there is no opportunity to radial lamellae to reorganize themselves again so that the single melting peak represents the true melting point of the existing lamellae in the sample.

Conclusions

On the basis of the results presented above its clear that the α_1-spherulites can be transformed to α_2-spherulites by heating above 145°C, also we can see that β-spherulites can transform to α-type spherulites if the sample of isotactic polypropylene is quenched from the isothermal crystallization temperature in cold water then reheated again, upon reheating β-spherulites transforms into α-form.

For samples crystallized in two steps, it was found that for example if the sample was crystallized at 140°C for a long time it shows two melting peaks. However, if the sample crystallized at 140°C then annealed at 155°C, it still shows double melting peaks upon melting due to reorganization. However if the same sample annealed at 160°C then heated directly it shows only one melting peak due to suppression of reorganization.

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