

CHAPTER 2

LITERATURE REVIEW



2.1 Isotactic Polypropylene

Isotactic polypropylene (iPP) is one of the most widely used polymer. Its value and significance originally stem from both commercial and scientific viewpoint, which are primarily related to the iPP's morphology studies. It was reported during the late 1950s by Natta and Corradini¹ that the chain conformation of iPP is a threefold(3₁)helix, which can be either right or left-handed, with a periodicity of 6.50 °A . The position of the methyl group(CH₃)with respect to the chain axis can be either up or down. As a consequence, four possibilities relative to a reference axis can be determined for a three-fold helix of iPP in the crystalline state as shown in Figure 2.1.

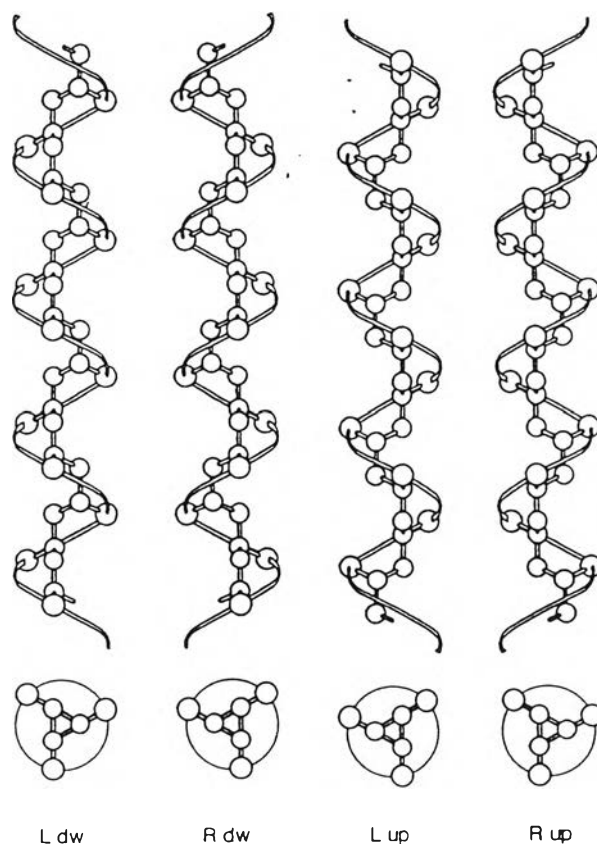


Figure 2.1 Chain configurations in isotactic polypropylene.

On the crystal lattice level, iPP exhibits three different morphological forms, normally α , β and γ . These three crystal forms are their arrangement chains. Each of these forms is identified with specific peaks in the X-ray pattern as shown in Figure 2.2. Another form of iPP with a degree of order between crystalline and amorphous phase was first reported by Natta² and Corradini, who named it the "smectic" form.

It has been well known that iPP forms lamellar structures when being crystallized either from the melt or from dilute solution, regardless of whether it is crystallized under quiescent or stress-induced conditions. Lamellae are defined as ordered structures that contain polymer molecules fold back and forth on themselves to some degree to form lamellae. The radial growth of iPP lamellae is usually in the form of spherulites or discs. In general, crystallization process consist of two major step : 1) primary crystallization and 2) secondary crystallization. In the primary crystallization, the growing lamellae evolve from a nucleus through sheaf-like structures into the growing spherulite. Growth continues until the spherulites come into contact with each other, or impinge. The growth fronts of the spherulites finally result in a multitude of polygonal formations confined by straight or curved line (Figure2.3). Secondary crystallization occurs within the spherulite, transforming a portion of the interlamellar material into crystalline material.

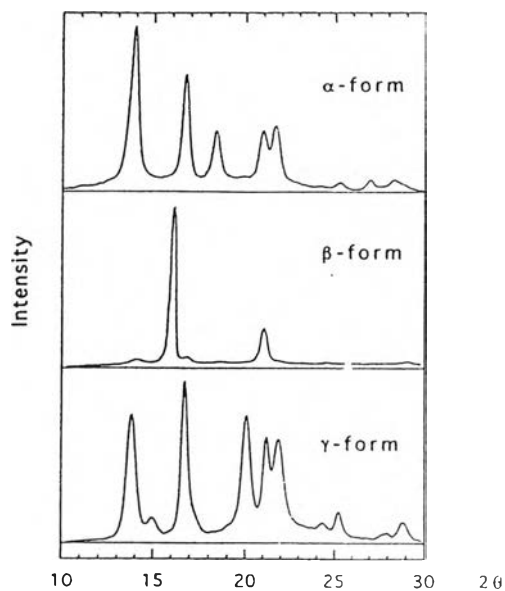
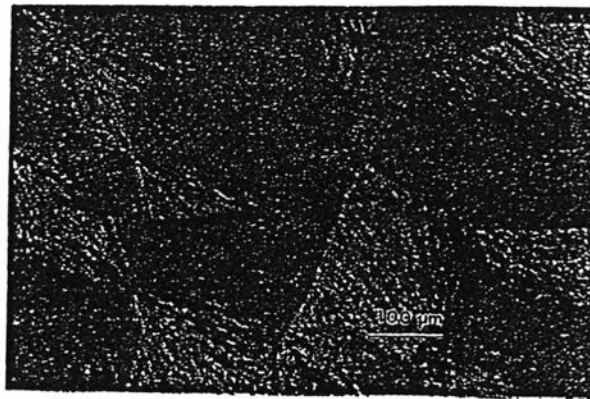
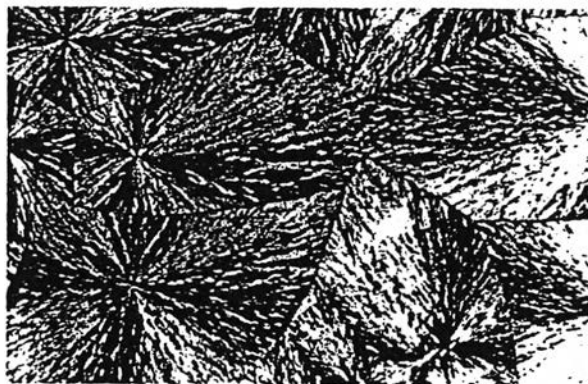


Figure 2.2 Wide Angle X-ray Diffraction(WAXD) of different morphological forms

The complex arrangement of lamellae within a spherulite is also a unique morphological feature of iPP. Under certain conditions, iPP has been shown to produce branches at an angle of 80° , as shown schematically in Figure 2.4 and optically in Figure 2.5. These branches are sometimes called "crosshatched" lamellae. The mechanism for the radial-tangential branching observed in iPP was explained by Lotz and Wittmann.³ Important structure is based on epitaxial growth of the tangential lamella on the radial one, due to crystallographic and structure interactions. This branching may have specific arrangement known as "quadrite" consisting of inter woven arrays of single crystal laths oriented at a fixed angle of 80° to one another.



(a)



(b)

Figure 2.3 Impingement of spherulite. The contact between adjacent spherulites is either straight or curved line. (a) Top picture is taken using $\frac{1}{4}$ wave plate under cross polar condition and (b) without $\frac{1}{4}$ wave plate (red filter)

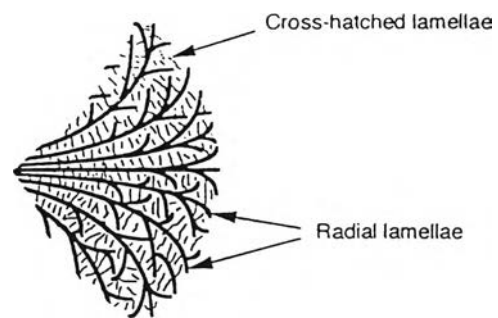


Figure 2.4 Schematic representation of branching and crosshatching in isotactic polypropylene.



(a)



(b)

Figure 2.5 Optical observation of branching in α -IPP.(a)with red filter(b) without red filter.

Furthermore, iPP crystals have been known to induce epitaxial crystallization of a number of polymers with their chain axes tilted at large angles (40-80°) relative to the helical axis direction present in the iPP substrate. For example, epitaxial growth of polyethylene on iPP substrate or vice versa has been studied by many authors⁴. Homoepitaxy with an 80° tilt angle of iPP, where different chain axis directions coexist within the same lattice, was proposed by Bruckner and Meille for the explanation of the γ crystal structure⁵. Using depolarizing light microscopy, several types of spherulite can be distinguished. In principle, the polarizing microscopic pattern of a spherulite shows a central dark cross (Maltese cross) with wings coincident with the respective planes of polarizer and analyzer. Depending on the birefringence, spherulites can be optically positive or negative. The birefringence of a spherulite, Δn , is defined as in Equation 1

$$\Delta n = n_r - n_t \quad \dots\dots\dots(1)$$

where n_r and n_t are the refractive indices along the radial and tangential direction of the spherulite, respectively.

The sign of birefringence of the spherulites can be determined by means of a primary red filter (λ - plate) located diagonally between crossed poles. When a spherulite is positive, its first and third quarter are blue (dark gray in a black and white picture) and the second and fourth ones are yellow (bright gray in black and white picture) (Figure 2.6a), whereas a reversed arrangement of the quarters is observed for a negative spherulite (Figure 2.6b).

Furthermore, based on the features of lamellae, the spherulite can be radial or ringed type. In radial spherulites the lamellae are straight, but in the ringed ones they are twisted around their longitudinal axes in a helical form. Under a cross polarized medium, concentric dark rings appear corresponding to the pitch of the helix.

The iPP exhibits a variety of spherulite type classified typically on the basis of the sign of the birefringence. The first attempt to describe the different morphologies of melt-crystallized iPP was carried out by Padden and Keith in 1959.⁶ When iPP was crystallized in the temperature range of 110-148 °C, five distinct types of spherulites exhibiting different optical properties were identified, as shown in Table 2.1. Among these three types exhibit slightly positive, negative and mixed birefringence revealed. The other two common types display negative birefringence which is characteristics of β -iPP spherulite.

One is radial and the other is a ringed type spherulite. The temperature ranges indicated in Table 2.1 for the formation of each type of spherulite should not be regarded as rigid values but rather trends.

The following sub-section in this thesis will further describe four major different crystallographic forms of iPP, namely α , β , γ and smectic forms.

2.1.1 α -FORM

The predominant crystal structure of pure (without nucleating agent) iPP, at atmospheric pressure, is the monoclinic α structure. In 1960, Natta and Corradini² calculated the unit cell parameters of the monoclinic α -iPP, which contains four three-fold helical chains,

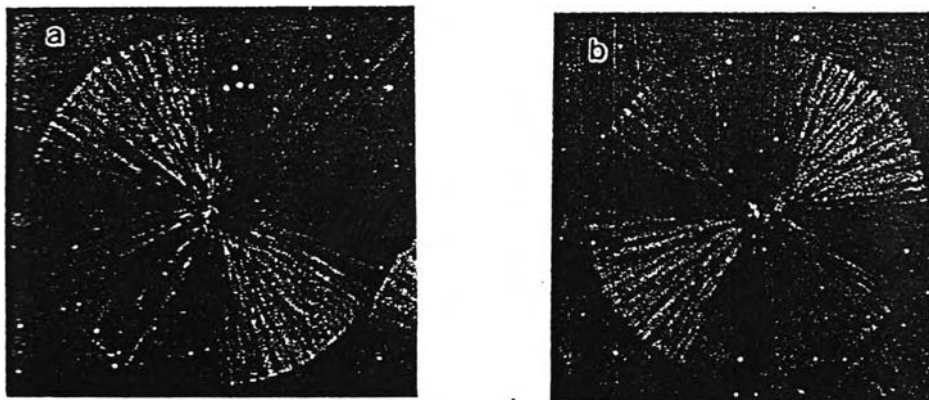


Figure 2.6 The sign of birefringence of spherulites: (a) positive (b) negative

Table 2.1. Classification of Polypropylene Spherulites According Keith and Padden

	Spherulite type				
	I	Mixed	II	III	IV
Crystal structure	α	α	α	β	β radial ringed
Sign of birefringence	+	+	-	-	-
Crystallization temperature ($^{\circ}\text{C}$)	<132	130-140	>138	<128	128-135

Source: Reference 6.

Where a, b and c represent the side of unit cell parameters and α , β and γ represent the angle between bc, ac and ab to be: $a = 6.65 \text{ \AA}$, $b = 20.96 \text{ \AA}$, and $c = 6.50 \text{ \AA}$, with $\alpha = \gamma = 90^{\circ}$, and $\beta = 99.3^{\circ}$. Later studies by Hikosaka and Seto reinvestigated the crystal structure of α -iPP.⁷ Their analyses and Mencik's show the crystalline structure of α -iPP in various degrees of disorder in the up and down positioning of the chains, depending on the thermal and mechanical history of the sample. Analysis of chain folding in the crystalline structure of α -iPP by Petraccone et al. revealed factor governing the configurational characteristics of polymer stems.⁸ However, the unit cell dimensions and the ordered arrangement of threefold right- and left-handed helices within the cell remain substantially unchanged

Table 2.2. Lattice Parameters of α -Form iPP

Bravais lattice	Lattice parameter (\AA)	No. repeat unit	Density (g/cm^3)	references
	$a = 6.65$ $b = 20.96$ $c = 6.50$ $\beta = 99.3^{\circ}$ $\alpha = \gamma = 90^{\circ}$	12	0.938	2
Monoclinic	$a = 6.66$ $b = 20.78$ $c = 6.495$ $\beta = 99.62^{\circ}$ $\alpha = \gamma = 90^{\circ}$	12	0.946	9

Table 2.2 (Continued)

Bravais lattice	Lattice parameter($^{\circ}$ A)	No. repeat unit	Density(g/cm^3)	references
	a = 6.67	12	0.937	9
	b = 20.94			
	c = 6.495			
	$\beta = 99.62^{\circ}$			
	$\alpha = \gamma = 90^{\circ}$			

Different unit cell parameters for the monoclinic α -iPP were also given by Turner-Jones as shown in Table 2.2.⁹

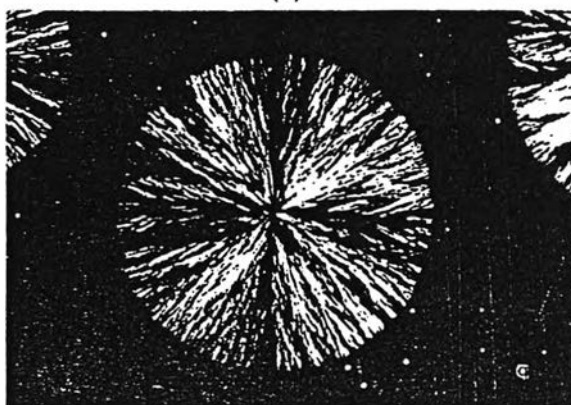
The spherulitic morphology observed in melt-crystallized iPP was first reported by Padden and Keith who classified the spherulites with respect to their birefringence.⁶ The α form of iPP exhibits 3 types of spherulites: 1) positive birefringence (α_+) 2) negative birefringence (α_-), 3) mix birefringence (α_{III} or α_{m}). Positive birefringence spherulites (α_+) can be developed at an isothermal crystallization temperature below 132°C (Figure 2.7). Negative birefringence spherulites (α_-) exist at a crystallization temperature greater than 138°C (Figure 2.8). However, the most common spherulites are of mixed birefringence type (α_{III} or α_{m}); they possess no distinct Maltese cross and are revealed as radiating arrays of intermingled areas of positive and negative birefringence (Figure 2.9). This type of spherulite has been observed at any temperature up to 150°C . The presence or absence of one type depends not only on the crystallization temperature but also on the film thickness.

The birefringence change of the α form spherulites has been directly related to the relative amounts of tangential lamellae, branching, inside the spherulites. Norton and Keller were able to prove that in the positively birefringent spherulites, α_+ , the amount of branching lamellae is relatively higher than that of the negatively birefringent α_- .¹⁰ It has been established that the proportion of the crosshatching phenomenon is reduced as the crystallization temperature increases until 160°C above which only radially splaying lathlike lamellae develop. Thus for low crystallization temperature or below 132°C , spherulites have high tangential lamellar content. Khoury estimated the angle between branched lamellae for twin crystals grown by crystallization in solution to be $\approx 80^{\circ}$.¹⁷ This

was in good agreement with electron microscopy results¹¹ and with other observations¹²



(a)



(b)

Figure 2.7. Positive birefringence spherulites α_1 , prepared at isothermal crystallization temperature of 115 °C. (a) With red filter (1/4 wave plate) and (b) without red filter.

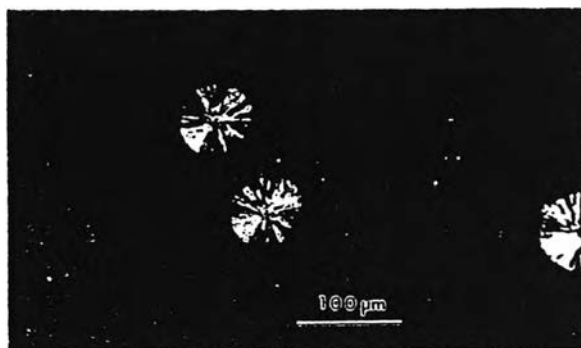


Figure 2.8. Negative birefringence spherulites α_{II} , prepared at isothermal crystallization temperature of 140 °C.

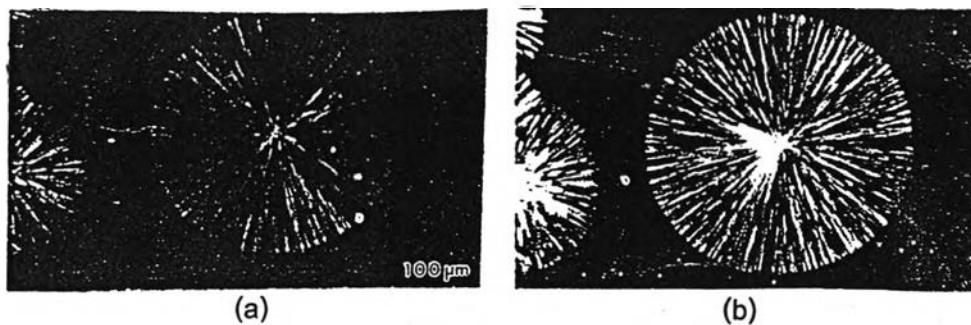


Figure 2.9. Mixed birefringence spherulites α_m prepared at T_c of 120 °C (a) With red filter and (b) without red filter.

The melting behavior of spherulites of polypropylene is complicated by the presence of thin lamellar branches inclined at 80° to the dominant radial lamellae. During a heating cycle the branches melt at a lower temperature than the dominant lamellae, causing an increase in the birefringence of the spherulites and, hence, of the specimen (Figure 2.10). Consequently, during melting a positive α_r - or a mixed α_m spherulite becomes negative as demonstrated in Figures 2.11 and 2.10C respectively. When the radial lamellae melt, the expected decrease in birefringence occurs, permitting an estimate of the melting point to be made as the temperature at which zero birefringence is attained (Figure 2.10). The temperature which have zero birefringence was increased due to lamellar thickening. Mezghani et al, demonstrated that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of the equilibrium melting point, T_m .¹³

Values of T_m for α -form reported in the literature fall into two groups, at around 186 °C and the other around 210 °C . Krigbaum and Miller determined T_m° to be 186 ± 2 °C, whereas T_m of 208 °C was reveal by Monnasse and Fatou¹⁴ . Kamide and Yamaguchi observed changes in melting temperature with crystallization time for different molecular weights and fractions of iPP.¹⁵ They noticed that at the same crystallization temperature the degree of shift of melting point is increased. The degree of shift is proportional to the crystallization time. At the end of their analysis they concluded that the changes in melting temperature with time were independent of molecular weight and its distribution. A few years later, independent studies by Mezghani et al. Using depolarized light microscopy led to T_m of α -form iPP was about 186.1 °C¹³.

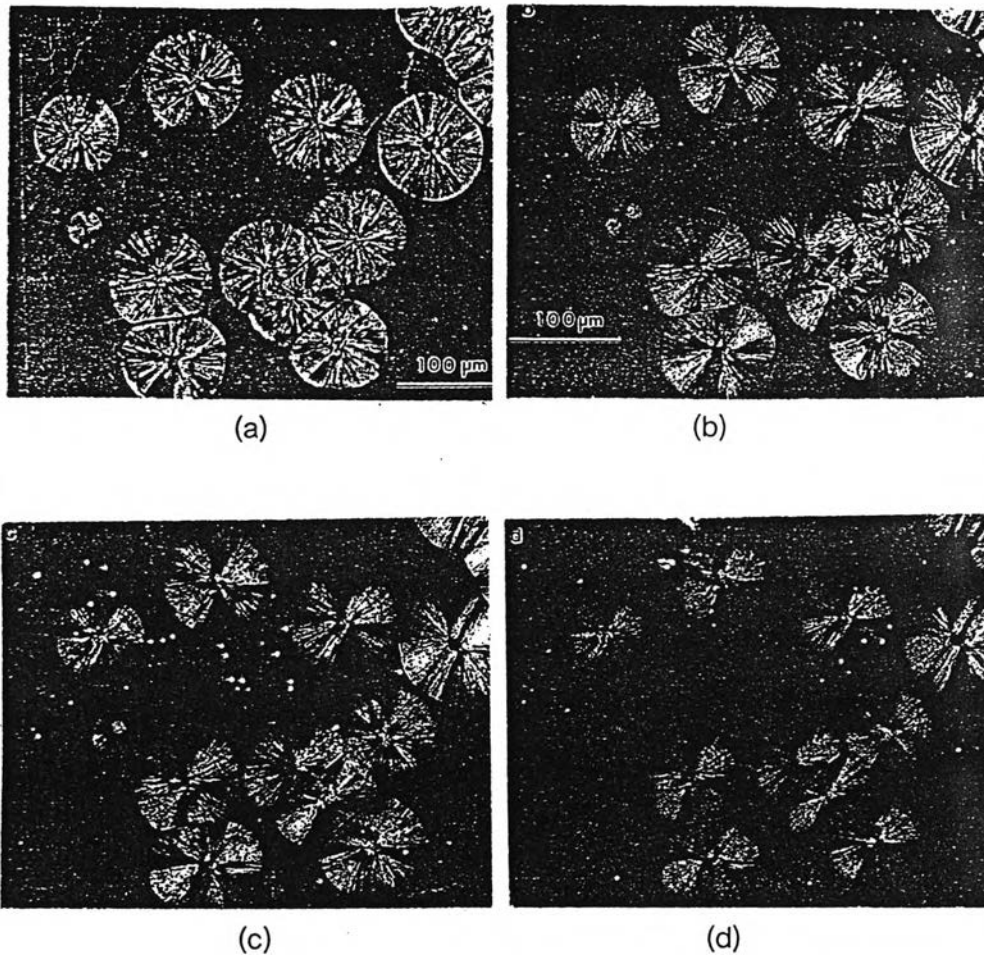


Figure 2.10. (a) Mixed birefringence spherulites α_m crystallized at $T_c = 145$ During melting the sign of birefringence becomes negative. (b) $T = 166$ °C; (c) $T = 168$ °C; (d) $T = 172$ °C

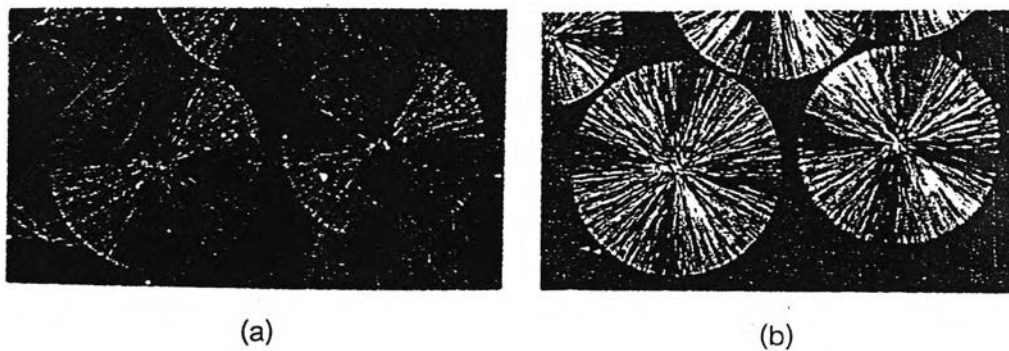


Figure 2.11. During melting the positive birefringence spherulites α_1 (see Figure 2.7) becomes negative. (a) With red filter and (b) without red filter.

2.1.2 β -FORM

The β -form is one of the crystal structures of the iPP. The β -form is hexagonal structure as explained in previous section. The β -form of isotactic polypropylene was first identified in 1959 by Keith et al.¹⁶ In his investigation, a small amount of β -form occurs sporadically at high supercoolings ($T_c < 130$ °C) or in quenched samples. However, under special crystallization conditions, when the temperature gradient method is used¹⁷ or when selective β -nucleating agents are present, a high amount of β -form can be produced. For example, quinacridone dyes or triphenodithiazine are β -nucleating agents widely known to produce up to 100% of the β -form under the appropriate thermal conditions of crystallization.¹⁸ The same nucleants were also used to produce lamellar single crystals of the β -form, The desired lamellar single crystals could be obtained either by melting followed by slow-cooling iPP thin films as reported by Geil,¹⁹ or by quenching a 5% iPP solution in paraffin wax from 210 to 100 °C as described by Turner-Jones and Cobbold.²⁰

The β form is normally referred to as "hexagonal iPP", characterized mainly by two X-ray reflections at interplanar spacing (d) of $d=5.53$ and $d=4.17$ °Å. In addition to these two diffractions, approximately 15 others of the β -form were identified. The exact unit cell of the β -form has not been resolved since oriented fibers were not obtained since conversion of β to α -form takes place upon drawing. The derivation of the unit cell of the β -form of unoriented specimens has been attempted by many researchers as shown in Table 2.3. Keith et al. suggested a four-chain unit cell with $a = b = 12.74$ °Å and $c = 6.35$ °Å.¹⁶

However, according to Addink and Beintema this model implies excessively close methyl interactions (3.6 °Å)²¹. Turner-Jones et al. noticed that a considerable fraction of all the observed diffraction maxima can be accounted for by a hexagonal (or trigonal) lattice with $a=b=6.36$ °Å and $c=6.49$ °Å.²⁰ Consequently, this cell can be recognized as the basic sub-cell of the β -structure. All investigations in the more recent literature agree well with this basic model. However, when these reflections are taken into consideration, this model is not sufficient. A more satisfactory model is the hexagonal with $a=b=11.03$

$^{\circ}\text{A}$ and $c=6.49^{\circ}\text{A}$. Another possible unit cell, suggested by Turner-Jones and supported by Meille et al., is the orthorhombic with $a=11.03^{\circ}\text{A}$, $b=19.10^{\circ}\text{A}$ and $c=6.49^{\circ}\text{A}$.⁵² The packing of the helical chains in the unit cell was suggested to be unidirectional (left or right). The calculated density of the one-chain hexagonal unit cell is 0.92 g/cm^3 .²⁰

Table 2.3. Lattice Parameters of β -form iPP

Bravais lattice	Lattice parameters ($^{\circ}\text{A}$)	No. repeat unit	Density (g/cm^3)	References	
Hexagonal or trigonal	$a=6.36$	3	0.92	8	
	$a=11.01$	9		9	
	$a=12.72$	12		58	
b=a, c=6.49, $\gamma=120^{\circ}$, $\alpha=\beta=90^{\circ}$	$a=19.08$	27	0.92	9	
	$a=22.03$	36		9	
	$a=25.43$	48		9	
Orthorhombic	$a=6.36$ $b=11.01$ $c=6.49$	6	0.92	58	
	$a=19.08$ $b=11.01$ $c=6.49$	18			9
	$a=12.72$ $b=22.03$ $c=6.49$	24			9

When crystallized from the melt the β form of iPP displays a strong negative birefringence as commonly observed in polymer spherulites. According to Padden and Keith, two types of β spherulite were developed sporadically with the α form.⁶ The first type is highly birefringent and is called negative radial, which grows below 128°C (Figure 2.12). The second type, negative ringed, is observed between 128 and 135°C (Figure 2.13). The different temperature ranges for the formation of a particular type of spherulite have been reported, due to the variability in the characteristics of the molecular structure of iPP studied.²² More detailed studies of the β spherulites were accomplished by Samuels.²³ His studies revealed that the β form consists of broad, locally parallel stacked lamellae just as in spherulites of other polymers, and the radial-tangential

lamellar arrangement does not exist for the β form. In short, all findings indicate that β -iPP lamellar crystals do not share either the peculiar lathlike shape or the branching morphology of α -iPP crystals.

In general, the growth rate of the β form exceeds that of the α form, while its melting point is in the range 145-150 °C which is, much lower than that of the α form (180 °C) (Figure 2.14). Like the α form, many values of the equilibrium melting point for β -form have been reported; it varies between 170 and 200. Recently, Mezghani and Phillips reported the T_m value of 174.4 °C for the β form using the same procedure for determining the most accurate value T_m of the α form.²⁴

The transition of the β form to the α form was also investigated by X-ray diffraction studies performed at different temperatures.

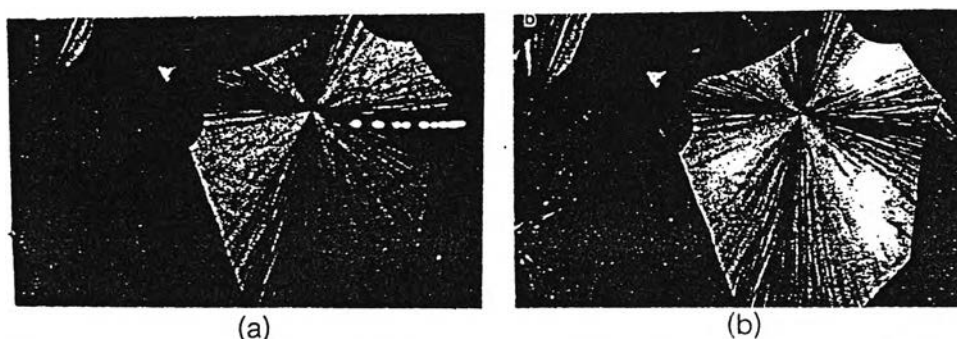


Figure 2.12. Negative radial β spherulites surrounded by mixed type α spherulites crystallized at 115 °C. (a) With red filter (1/4 wave plate) and (b) without red filter.

According to Varga, when heating begins from the temperature of crystallization the β form does not recrystallize into the α form²⁵. Instead, it melts separately as shown in Figure 2.14. However, if samples containing the β form are cooled below a critical temperature T_R^* before heating, partial melting is accompanied by recrystallization into the α form. T_R^* is in the range of ~100-110 °C. Since the β form contains only unidirectional helices, contrary to the α form which is packed with alternating right and left helical chains, the β to α transition requires rewinding of chains. In the solid state this directional change is impossible; therefore, for β to α transformation requires partial melting of the β form. The mechanisms which create α form nuclei on partial melting of

β spherulites were also investigated by Fillon et al. using thermal analysis and optical and electron microscopy²⁶.

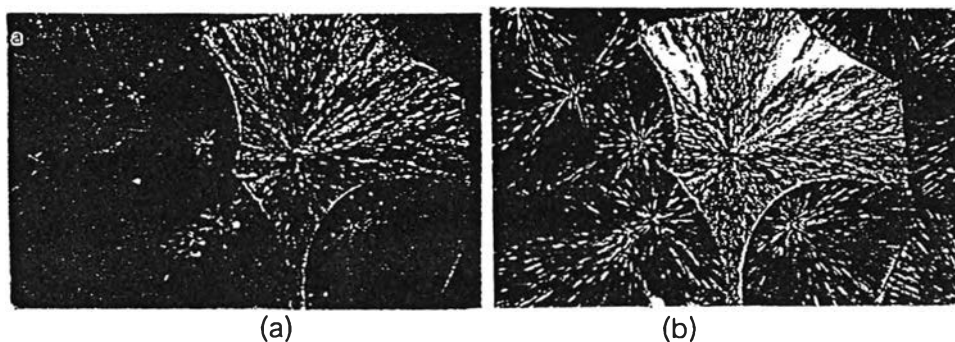


Figure 2.13. Negative ringed β spherulites isothermally crystallized in 0.5% propylene-ethylene copolymer at 120 °C. (a) With red filter (1/4 wave plate) and (b) without red filter.

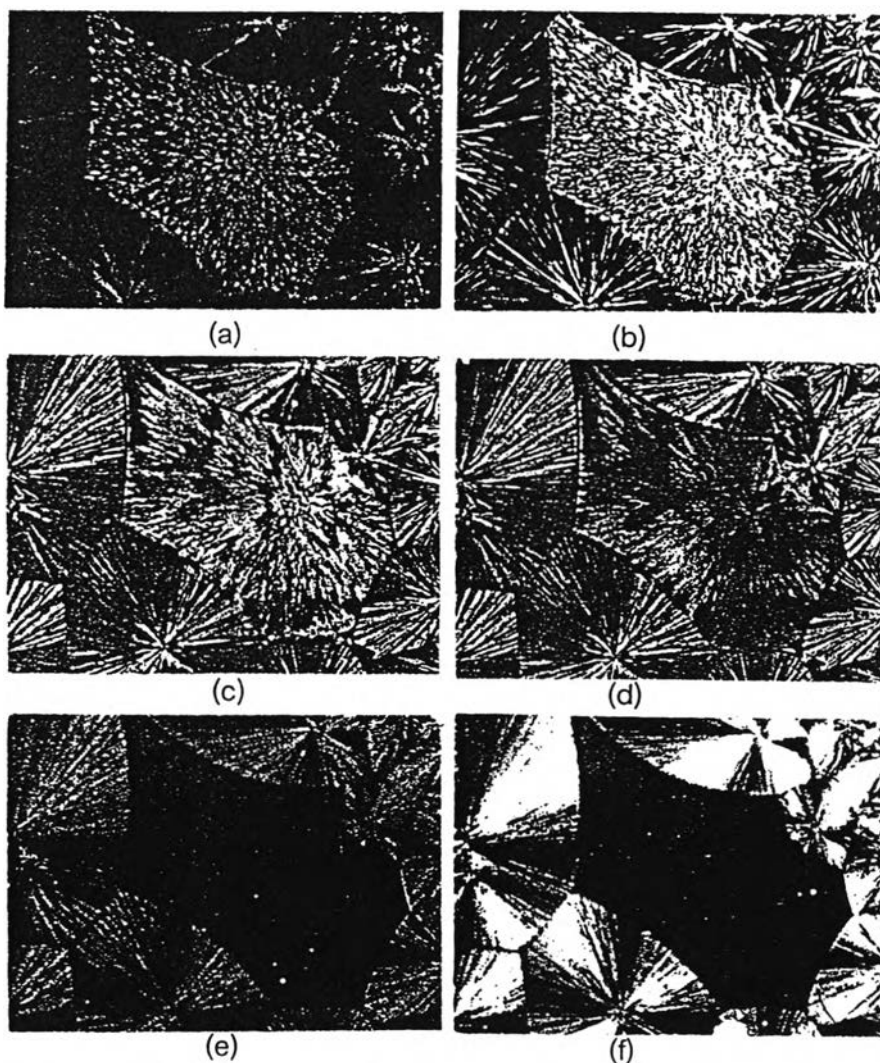


Figure 2.14 Morphological changes of the β form during melting. (a) the β form at $T_c = 120^\circ$ surrounded by mixed-type α form. (b) same as (a) without red filter (c), (d), and (e) during melting; (f) same as (e) without red filter. The β form melt first.

2.1.3 γ -FORM

The γ -form is also another crystal structure of the iPP. The γ -form is triclinic structure. The γ -form of iPP was first noted during the 1960s and was generated by several methods²⁷. It was largely produced by crystallization at elevated pressures. However, under specific conditions, low molecular weight fractions ($M_w < 6000$) of iPP can be used to generate γ form or even single crystals. Another procedure of γ -iPP formation is crystallization from the melt of high molecular weight stereoblock copolymer with small amounts (3 to 10%) of ethylene. It appears, that the presence of interruption, rather than the specific nature of the interruptions, of isotacticity is the main feature promoting the γ crystallization at atmospheric pressure.

Early studies mainly involved the formation of the γ phase by introducing chemical heterogeneity in the polypropylene chain caused by atacticity or by copolymerization²⁸. A new study demonstrates that the γ phase is produced at elevated pressures from high molecular weight homopolymers and the developed γ phase has the same diffraction patterns as the low molecular weight polymers. This study has also confirmed that the γ phase is not the result of some unexpected degradation reaction at elevated pressures. Turner-Jones considered some copolymers of propylene with ethylene (as well as other co monomers) and found that the presence of a comonomer enhanced the formation of the γ phase²⁸. The polymers at that time contained atactic material, and there was no a priori way of separating the effects of atacticity from the effects of copolymerization, which would be complementary. Polymers available now have > 99% isotacticity and so the effect of the microstructural variables can be separated. More recent studies conducted by Mezghani and Phillips²⁴, using variable amounts of ethylene content in >98% isotactic propylene copolymers, confirmed the results reported by Turner-Jones²⁸ and also indicated that the amount of the γ form is proportional to the ethylene content and to the crystallization temperature. Accordingly, the amount of the γ form is higher at low supercoolings.

When the pressure is varied, only the α and γ forms are observed²⁹. As the crystallization pressure increases the γ form start to coexist with the α form until it

becomes dominant at 2 kbar²⁹. Furthermore, it appears from experiment that the lower the supercooling, the higher the amount of γ form produced at a specific pressure³⁰.

Like β form, all attempts at obtaining oriented fibers of γ phase resulted in a transformation into the oriented α crystals. Consequently, all the X-ray diffraction data available in the literature are obtained either from powder or bulk samples, although diffraction patterns from γ single crystals have been reported.³¹

Table 2.4. Lattice Parameters of γ -Form iPP

Bravais lattice	Lattice			
	Parameter (Å)	No.repeat units	Density (g/cm ³)	References
Triclinic	a=6.54 b=21.40 c=6.50 $\alpha=89.0^\circ$ $\beta=99.6^\circ$ $\gamma=99.0^\circ$	12	0.946	87
	a=6.55 b=21.57 c=6.55 $\alpha=97.4^\circ$ $\beta=98.8^\circ$ $\gamma=97.4^\circ$	12	0.935	34.35
Orthorhombic (Fddd, Fdd2)	a=8.54 b=9.93 c=42.41	48	0.933	34.35.97

The γ form was first identified as triclinic with the unit cell similar to that of the α form, with a slip along the c-axis direction ($a=6.54^\circ\text{A}$, $b=21.40^\circ\text{A}$, $c=6.50^\circ\text{A}$, $\alpha=89^\circ$, $\beta=99.6^\circ$, $\gamma=99^\circ$)³². Recent studies of a γ -form generated at atmospheric pressure from low molecular weight iPP ($M_n=6300$) have led to a reassignment of the structure as a face-centered orthorhombic unit cell. The lattice parameters of such orthorhombic cell are $a=8.54^\circ\text{A}$, $b=9.93^\circ\text{A}$, and $c=42.41^\circ\text{A}$ (Table 2.4). The new structure accounts for the diffraction pattern in a more satisfying manner than earlier structure. Figure 2.15 represents a schematic arrangement of chain stems in the γ orthorhombic unit cell. The new structure is unique in that it contains sheet of parallel molecules, but the molecular

orientation between adjacent sheet becomes nonparallel every two sheets. The angle between the nonparallel stems is about 81° .

On the spherulitic level, pure γ form shows negative birefringence as shown in Figure 2.16. It is clear from Figure 2.17 that the lathlike structure of the α form is absent in the γ spherulites. However, when α and γ form are present in the same sample the morphological features become complex. The optical studies of microtomed sections as reported by Campbell and Phillips²⁹ show no evidence of Maltese cross formation when less than 10% of the material is in the γ form,

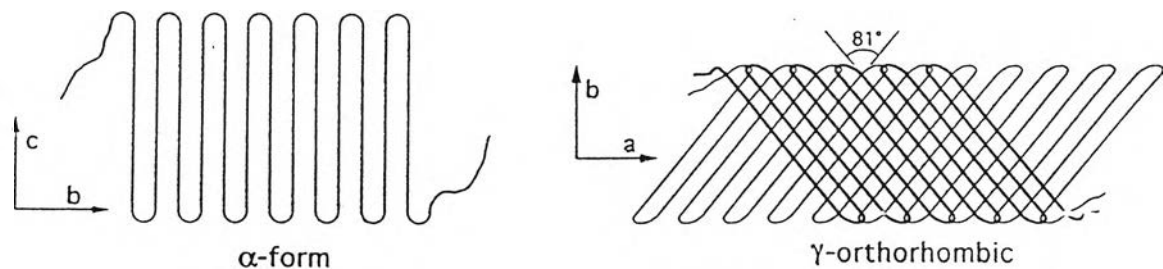


Figure 2.15. Schematic arrangement of chain stems in the α -monoclinic and the γ orthorhombic unit cells.

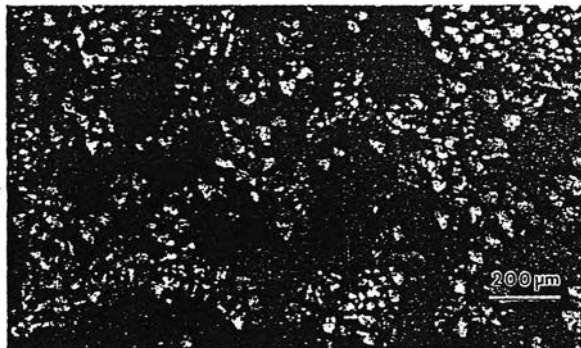


Figure 2.16. Spherulitic morphology of the γ form. Sample is isothermally crystallized at 200 MPa (2 kbar) and 187.5°C . The spherulites show negative birefringence.

However, when more than 60% γ form is present, a clear Maltese cross exists. In addition, optical and electron microscope studies of etched specimens reveal no crosshatching in specimens with $> 60\% \gamma$ crystals.

The studies of Morrow and Newman, of low molecular weight ($M_n=1260$), show that solution-crystallized iPP gives rise to needlelike crystals with the presence of both α and γ form structures.³² This morphology is also observed for high molecular weight samples crystallized at 125 MPa (1.25 kbar) where the α form coexists in small amount with the γ form. The contact faces of epitaxially crystallized γ on α substrates has been investigated by Stocker and coworkers, using electron microscopy and atomic force microscopy.³³ The results show that the contact face with a low density of methyl side chains is preferred over the alternate face with a higher density of methyl groups.

The coexistence of the α and γ phases at high pressures can be predicted from their thermodynamics parameter differences. Calculated value of the Gibbs free energy (ΔG) plotted for both α and γ phases as a function of temperature show that at low supercooling the ΔG of the γ form is lower than that of the α form. The experimental results are in good agreement with the theoretical predictions.³⁴ The γ phase may be less stable at atmospheric pressure because of its being of an intrinsically higher entropy form than the α phase. The melting point of the γ form is mostly reported in the range from 125 to 150°C for low molecular weight samples. In the case of pressure-crystallized samples with high molecular weight iPP, the melting occurs above 150°C.

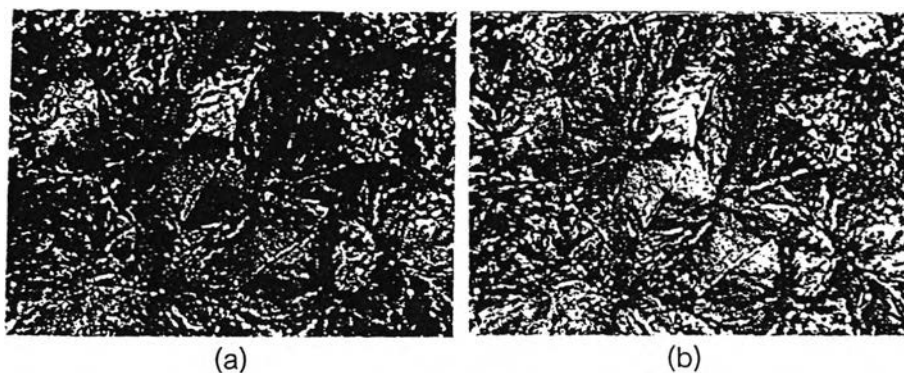


Figure 2.17. The γ -spherulites, isothermally crystallized at 200 MPa (2 kbar) and 187.5 °C, show no lathlike structure of the α form. (a) with red filter (1/4 wave plate); (b) without red filter.

The results of melting at high pressures show that the equilibrium melting point of iPP is linearly proportional to the pressure. The equilibrium melting point of the γ form at atmospheric pressure is the intercept of the line and has a value of 187.6 °C.³⁴ This value is in good agreement with the equilibrium melting point determined from the melting temperature versus l/l (lamellar thickness), where 100% γ samples were prepared at 2 kbar and melted at atmospheric pressure.

2.1.4 Smectic

The smectic form is an intermediate crystalline order. This mesomorphic form was first named by Natta et al, and was later assigned different names² such as Miller suggested that the order existing in this form might be of the type described in general terms by Hosemann as "paracrystalline".³⁵ This term was also used by Zannetti et al. and Wunderlich while Grebowicz proposed the term "condis crystal," which means conformational disordered crystal.³⁷

The preparation of this form is very simple: quenching thin sheets of iPP from the melt into ice water. The main characteristics of this mesomorphic form are indicated by two broad maxima X-ray diffraction, one at 14.8° and the other at 21.2° (2θ , $C_{\nu}K_{\alpha}$). The interpretation of the structure formed is still disputed in the literature. Natta et al, claimed that this form is composed of bundles of parallel three fold helices, right and left-handed, where more order is present in the chain axes. In addition, the smectic form is transformable into the α form by annealing at temperatures higher than 70 °C. This fact led Bodor et al, to conclude that this form is composed of microcrystals of α -iPP. On the other hand, Gailey and Ralston and later Corradini et al, suggested that the smectic form contains small crystals of the β -iPP.³⁸ This suggestion is based on the position of the two maxima of the smectic form close to the position of the two most intense β peaks.

The density of the smectic form has been reported by Natta et al, to be 0.88 g/cm³, which is higher than that of atactic PP (0.85 g/cm³).

2.2 β -formation of iPP

Polymorphism is a well-known effect in crystalline isotactic polypropylene (iPP). In general, formation of iPP can involve different crystalline morphology including α , β , γ , and smectic. Of all these crystalline forms involved in the modification of iPP, the β -form demonstrates interesting performance such as higher values of elongation at break and higher impact strength. In addition, the β -form would convert into the α -form, consequently resulting in the formation of pinholes due to the lower density of the β -form than that of the α -form when the β -form iPP experiences an extension or heat treatment. We can take advantage of this transformation to produce a porous film. The textiles made of porous iPP exhibit a higher moisture uptake and a higher gas transport. These interesting characteristics suggest a potential practical applicability. Since β -iPP is a subject of interest in this study, a review on how β -iPP can be prepared will be detailed in the following sub-section.

2.2.1 Preparation of β -iPP

Commercial grades of iPP, when processed in laboratory or industrial scale normally crystallize essentially into the α -form. Early studies Padden³⁹ and colleagues demonstrated the formation of the α -iPP crystals which were also accompanied the appearance of the β -iPP crystal formation under high supercooling. They used X-ray diffractometry and optical microscopy to characterise both α and β crystal forms. Later studies by many investigators revealed similar observations to Padden's findings.

In conventional iPP samples, crystal structure of the β -phase was determined in very low content. The β -form contents was investigated by kx value that was explained by Turner Jones, Aizlewood and Beckett.⁴⁰ They introduced a kx value to be used for characterizing the proportion of β -form by X-ray diffractometric data. The kx can be calculated as follows :

$$k_x = \frac{H_{\beta_1}}{H_{\beta_1} + H_{\alpha_1} + H_{\alpha_2} + H_{\alpha_3}} \dots\dots\dots(2)$$

Where $H_{\alpha_1}, H_{\alpha_2}, H_{\alpha_3}$ are intensities of α -form diffraction corresponding to diffraction angles, θ , of $7.1^\circ, 8.5^\circ$, and 9.4° , respectively, and H_{β_1} is the intensity of β -diffraction peak corresponding to the angle θ of 8.1° . The k_x value is a relative measure for characterizing the polymorphic composition but does not express the absolute value of β -content numerically (even though its value is 0 for α -iPP and 1 for β -iPP). A k value of ≤ 0.85 was found for the samples prepared by Turner Jones, Aizlewood and Beckett⁴⁰. It is notable that polarized light microscopy (PLM) is also considered a relative quantification of the β -form since the peculiar high birefringence and types of β -form are different from those of the α -form⁴. Calorimetric melting curves also provide information about the polymorphic composition. However, melting of the β -form is a very complex process including pronounced melting memory effect. In fact, calorimetric curves give no exact information on the polymorphic composition unless the possibility of β to α -recrystallization is eliminated. This elimination can be maintained if samples containing β -iPP are never cooled below the critical temperature (T_R) that is the β to α transition temperature of 383K. It should be noted that all the calorimetric curves and thermo-optical micrographs were recorded under these conditions.

Several attempts were subsequently made to prepare the iPP in pure β form. Two methods have been used successfully to prepare samples rich in the β -form: the temperature gradient method⁴¹ and the introduction of β -nucleating agents⁴². It is also known that shear stress can promote the formation of the β -form. However, based on the literature review, pure β -iPP were hardly formed in most cases.

Studies by Verga and Colleagues⁴³ demonstrated that pure β -iPP could be prepared under laboratory. In their studies, iPP samples were blended with special pigment and stabilized using particular thermal conditions for the crystallization. The formation of pure β -phase was proved and confirmed by several characterization techniques including X-ray diffractometry (WAXD), polarizing optical microscopy and differential scanning calorimetry (DSC). Resulting X-ray diffractogram, morphology, and

DSC thermogram showing such β phase formation were included in Figure 2.18-2.20, respectively. More comprehensive investigations revealed that the formation of β -iPP had an upper and a lower (threshold) temperature, $T(\beta\alpha)$ or transition temperature from β to α and $T(\alpha\beta)$ or transition temperature from α to β . The transitions with reference to the experimental data will be later discussed.

$T(\alpha\beta)$ is the α to β transition temperature. At this temperature α -crystal fronts propagating into β -spherulite segments ($\alpha\beta$ -transition). Due to the higher growth rate of the β -phase it spreads over the total bulk of melt. On the other hand, $T(\beta\alpha)$ is the β to α transition temperature. At this temperature growth rate of α phase is higher than β phase and the appearance of α phase is higher than β phase.

Some important methods for the preparation of β -iPP rich samples or even pure β -iPP are described in the following sub sections. Although this method principally permits the formation of the pure β -phase, α -nuclei may accidentally emerge in the melt region, growing into α crystal form.

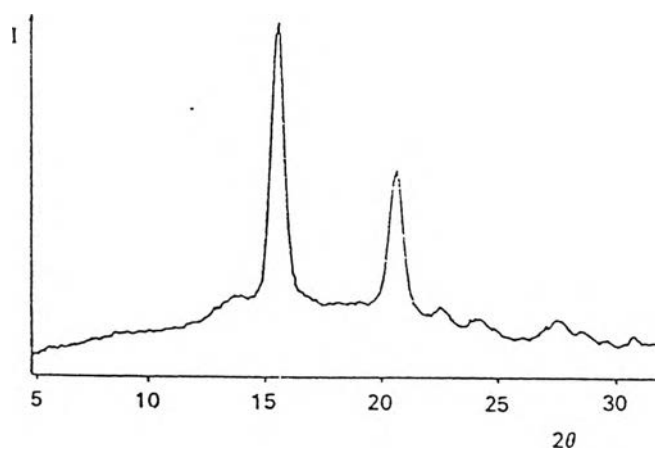


Figure 2.18 X-ray diffractogram of pure β -iPP⁴⁴

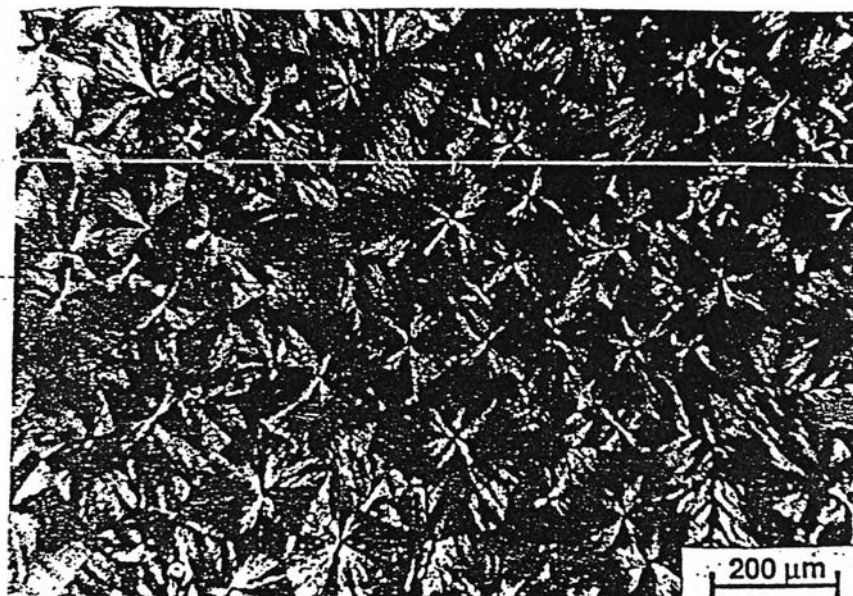


Figure 2.19 Optical micrograph of pure β -iPP crystallized at $T_c=398\text{ K}$ ⁴⁵

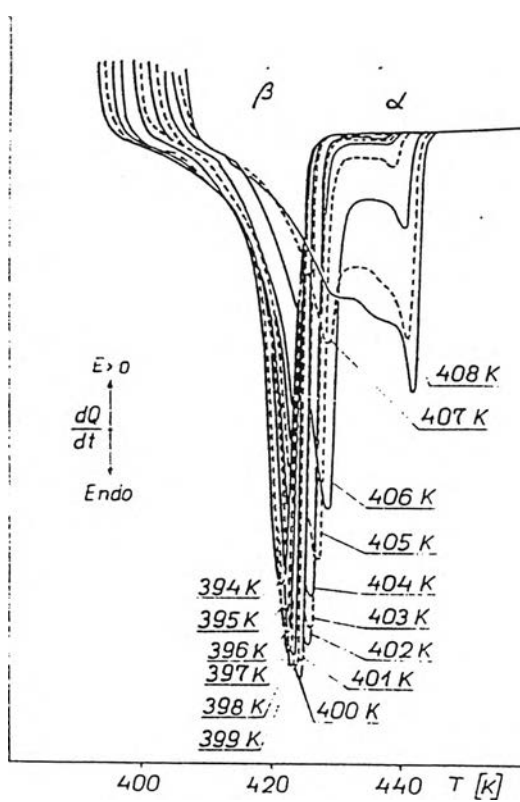


Figure 2.20 Melting curves of β -nucleated iPP samples crystallized at different temperatures plotted on a common baseline ($v_h=10\text{ K/min}$)⁴⁶

2.2.1.1 Temperature gradient method

Temperature gradient method is one method for producing β -form iPP. The temperature gradient crystallization method was studied and explained by Crissman⁴⁶, Kamida and Nakamura⁴⁷, Fujiwara⁴⁸ and Lovinger.⁴⁹ A thorough review of the temperature gradient technique was also given by Fujiwara.⁵⁰ This technique could be used to prepare small oriented β iPP films. The procedure is based on the appearance of β -nuclei on the surface of growing α -crystal fronts propagating into β -spherulite segments ($\alpha\beta$ -transition). Due to the higher growth rate of the β -phase, it spreads over the formation of pure β -phase, α -nuclei may accidentally emerge in the melt region, growing into α -spherulites situated in the continuous β -phase as teardrop-shaped inclusions. Film samples obtained in this way were used for determination of several peculiarities and characteristics of the structure and behaviour of the β -phase.

2.2.1.2 Addition of selective β -nucleating agents

Addition of selective β -nucleating agent is considered the most interesting method for β -formation of iPP. Its merit lies on the fact that β -phase formed by β -nucleating agent is more stable than that obtained using other method. Crystallization in the presence of β -nucleating agents promises the most reliable method for industrial applications. There are many β -nucleating agents used to promote β -form such as triphenol ditriazine, aluminium salt of quinizarin sulphonic acid, disodium and calcium salts of phthalic acid. However the most well known and widespread β -nucleating agent is a γ -quinacridone red pigment (Permanent Red E3B), which was first suggested by Leugering⁵¹ as an efficient β nucleating agent. This pigment was later used by several research groups.

The iPP samples crystallized in the presence of γ -quinacridone contain large amounts of the β -crystal content. The k_x values are around 0.8 as calculated from X-ray diffractometric data but, when crystallized under suitable thermal conditions, k may reach about 0.9. Even though γ -quinacridone is one of the most effective β -nucleating agent

but pure β -iPP could not be prepared. It was also observed that its activity is reduced during the processing. Therefore the processing condition is obviously the important parameter to controlling the activity of this β -nucleating agent. In the other word, γ -quinacridone has a disadvantage that is its intense red colour, which may restrict its practical application.

Due to the colour limitation of γ quinacridone, several researchers have attempted to develop the effective β -nucleating agent that has no colour. Garbarczik and Paukszta⁴² found that heterocyclic stabilizers, such as triphenol ditriazine, were also effective β -nucleating agents but the reported k_x value was approximately ≈ 0.3 . According to the literature, aluminium salt of quinizarin sulphonic acid, disodium and calcium salts of phthalic acid have β -nucleating activity.

Shi, Zhang and Jins⁵² revealed a very high β -nucleating activity for some two-component compounds obtained by the reactions of certain organic acid with CaCO_3 , but not defined unequivocally in their patent disclosure of their products of predominantly β -modification crystallized by means of their patented nucleating agents. They reported very high k_x values, even as high as 0.93. It has recently been observed that the mineral wollastonite (calcium silicate) is also active as a β -nucleating additive.

Varga and coworker⁵³ studied that the β -nucleating activities of Ca, Ba, Zn, Cd and Al salts of aliphatic and aromatic dicarboxylic and polycarboxylic acids. It was established that several Ca and Zn derivatives were very active while some Ba salts were moderately active β -nucleating agents. No Cd and Al derivatives were found to be active. Figure 2.21 and 2.22 show calorimetric melting curves for samples crystallized in the presence of some β -nucleating additives. It can be seen that Ca salts of pimelic, phthalic and pyromellitic acids have the highest nucleating activities, as proved by the presence of intensive β -peaks in the melting curves.

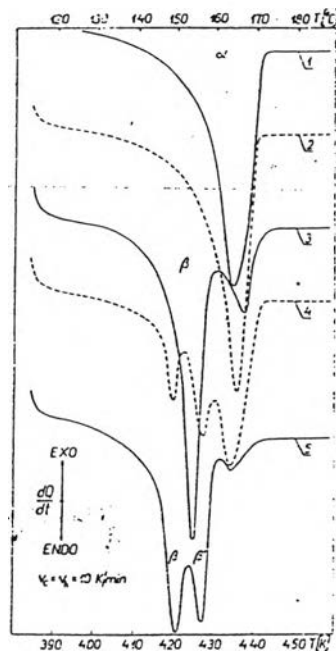


Figure 2.21 Melting curves of iPP samples (Tipplén H523) nucleated with Ca salts (1w/w %) of different organic acids ($V_c=10$ K/min, $V_h=10$ K/min, $T_R=383$ K): (1) original iPP; (2) benzoic; (3) phthalic; (4) terephthalic; (5) pyromellitic acid.

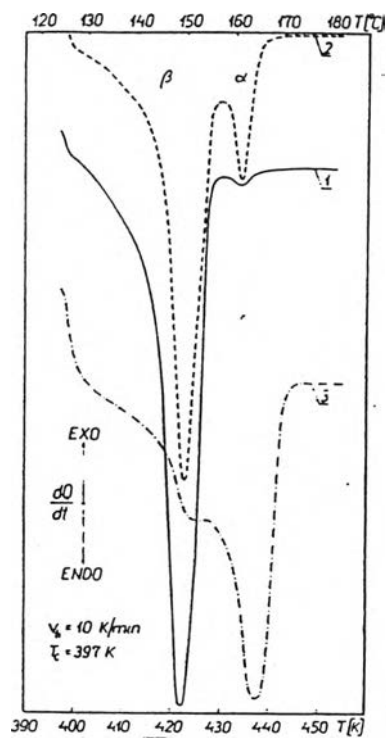


Figure 2.22 Melting curves of iPP samples (Tipplén H523) nucleated with different salts of pimelic acid ($T_c=397$ K, $V_h=10$ K/min): (1) Ca; (2) Zn; (3) Al.

It can be supposed upon these results that there may be a large number of β -nucleating agents (including selective ones), and that the discovery and introduction of further ones can be predicted. This supposition was supported by a comprehensive calorimetric essay on commercial iPP grades, some of which showed a high tendency to β -crystallization.

2.2.1.3 Crystallization in mechanically loaded melts

Crystallization in mechanically loaded melts is another method for nucleating β -form iPP. Mechanism of the crystallization under mechanical load involves the supermolecules of polymers which consist of two parts: 1) extended chains and 2) fold chains. Under a shear or strain stress, the molecular chains are extended and ordered into bands. These bands oriented in the direction of the mechanical loading can act as a nucleus of crystallization. This characteristic is named row nuclei. In the fold chains part, the molecular chains are positioned perpendicularly to the row nuclei.

2.3 Relationship of β -iPP to mechanical properties

In general, mechanical properties of iPP can be related to its polymer structure. In α -form iPP, the α crystal is essentially the monoclinic structure. The α form spherulites consist of an aggregate of lamellae that radiate from the central nucleus outward and have the amounts of tangential lamellae branching inside spherulite. This characteristic of iPP can relate directly to the resulting mechanical properties. Gerard Vigier⁵⁴ and his coworker explained that the presence of tangential crystallites in α spherulites, could result in a rigid "crosshatched" network which made the deformation of the amorphous component in the intercrystalline zone much more difficult. Therefore, such interlocked structure occurred in the α form spherulites reflect high modulus of elasticity, low ductility, and low elongation at break of the sample. On the other hand, they explained, that the mechanical properties of β iPP relate well to the hexagonal structure of the β crystal. The β -form spherulite has the amounts of sheaf-like structure. The sheaf-like structure

consists of parallel straced lamellae, tending to pack into bundles with the presence of sheaf-like structure in β iPP, sample having less interlocked tend to have low modulus of elasticity, high ductile, and high elongation at break. Thomus and co-worker⁵⁵ shown that β form iPP nucleated by trans-quinacridone dyeing, in the iPP was responsible for the significant modification of the impact resistance, result especially in a much higher ductility of this polymer. This result clearly shows the β spherulite morphology exhibits a significant influence on the impact properties . They also explained that polypropylene seemed to be very sensitive to the nucleating agent content (nucleating density), where very small change of the concentration provoked a dramatic decrease of the ductility. J.Karger-Kocsis⁵⁶ revealed the relationship of β to α transformation: on mechanical properties, using the PTT (Phase Transformation Toughening) occurred in β -iPP when it was stretched. Phase transformation toughening is a widely used concept for toughness improvement in metal and ceramics. PTT is featured by a mechanical stress-induced transformation from a metastable and, more densed structure to a more stable , and less densed crystalline modification. This transformation is associated with a specific volume increase . As a result, the transformation zone at the crack tip becomes subject to compressive stresses, due to which the crack growth is efficiently hindered (crack tip shielding mechanism). This concept become of interest also for polymers. Based on the results achieved on iPP ,that underwent β to α ($\beta\alpha$) transition during mechanical loading, it was claimed, that in semicrystalline polymer PTT is likely to work in the opposite direction. Toughness improvement of β -iPP was attributed to the development of a more perfect crystalline structure, including from (α -form), adapted to the local stress field, and to the formation of an enlarged (stress whitened) plastic zone. The $\beta\alpha$ -transformation in iPP is linked to a nominal contraction of -2.71% based on the crystallographic densities of the related modification (0.921 and 0.946 g/cm² for the β - and α iPP, respectively). A number of question merit further study in conection to the $\beta\alpha$ -phase transformation toughned iPP, such as the driving force of this transition and its efficiency as a function of fractional $\beta\alpha$ -conversion and mechanical loading frequency. Broda⁵⁷ and co-worker shown the result of research relating to incorporation of pigment (quinacridone pigment) in changing supermolecular structure of PP fiber. During fiber

formation, a partly crystalline fibrillar-lamellar structure was formed. In side fibrils the lamellar crystallites were aligned alternatingly with amorphous phase. In fiber containing quinacridone pigment, some β -crystals were created. In spite of high nucleating capacities of the pigment, the β content was not great. Because of pigment, the formed structure was more stable with less defect. However, in unsuitable condition processing, the β -form could not be nucleated. During fiber formation, pigment that were in the melt of crystallized polymer were force outside growing crystals. Particle of aggregated pigment with dimension comparable to thickness of fibrils located in interfibrillar zones. During fiber drawing, the fibrillation process occurs. It led to distinct separation of fibrills. Because of the low interfibrillar cohesion, which resulted from a small amount of connecting macromolecules and from weak interfibrillar bounding, the fibrillation process of PP fibers proceeded easily. During of fibrillation neighboring fibrils slide past one another and left vacancies behind them.

Under the influence of the localized stresses caused by defects, void will stretch perpendicularly to the fiber axis, separating bundle of fibrils. An irregular net with crazes appeared on the fiber surface. A craze can be defined as a zone spanned by aligned fibrils alternating with elongated voids, both being parallel to the draw axis. Pigments that were located in interfibrillar zone disturb in the reciprocal displacement of fibrils. Numerous places with localized stresses were formed with the presence of pigments. As a result, numerous lateral slot were formed with the presence of pigments, leading to a decreased strength of fiber.

2.4 Application of β -iPP

Polypropylene is a low-cost polymer of large scale production. Its high resistance to most of the conventional chemical and good mechanical properties. More specifically with β iPP, it offers higher elongation at break and toughness than other crystal formed iPP. Therefore, this could be a suitable crystalline form for producing the product which high toughness. Apart from pure β iPP, we can take advantage of $\beta\alpha$

transformation during processing or subsequent modification to produce a microporous film. Microporous films are one of the basic and important membrane product.

Most of the polymeric membranes are now prepared by using the solution cast, or-called phase inversion method. The structure and properties of the membranes can be changed by evaporation or subtraction of solvents in the gelation and solidification processes. However, the disadvantage of the solution method is that a large amount of waste solvents have to be dealt with and, the reuse of which is usually very difficult. .

A stretching method is an alternative method developed for preparing microporous membranes. Polypropylene microporous films obtained by this method are now commercially available under the trade name Celgard . The preparation procedure involves the consecutive steps of uniaxial cold stretching and hot stretching a non-porous semicrystalline film. The stretching method is economic and technologically convenient because no solvent are required. However, only a uniaxial stretching method has been successful for polypropylene so far and, as a result, the pore are slit-like in shape, and the anisotropy of films in mechanical properties is obvious. The tensile strength in the lateral direction is very low, only about 10 MPa, so the films are very easy to slit. These disadvantages limit the application in many important areas.