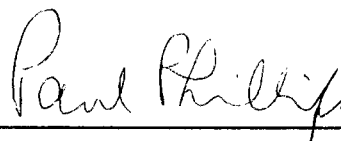


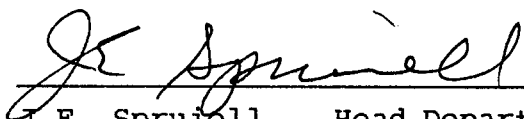
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I am submitting herewith a thesis written by Khaled Mezghani entitled "Isothermal Crystallization and Melting of Deuterated Isotactic Polypropylene." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

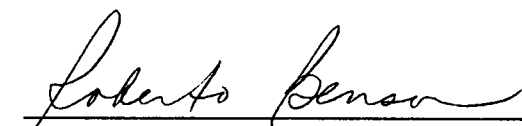


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Associate Vice Chancellor and
Dean of The Graduate School

**Isothermal Crystallization
and Melting of Deuterated
Isotactic Polypropylene**

A Thesis
Presented for the
Master of Science
Degree

The University of Tennessee, Knoxville

Khaled Mezghani

May 1995

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High regards and love to my mother, brothers, sisters, wife, and daughter for their continued encouragement and support.

DEDICATION

To my mother, brothers, and sisters.

To my wife and precious daughter.

ABSTRACT

The correct value of the equilibrium melting point of isotactic polypropylene has been determined using small angle x-ray diffraction. The conflict in the literature between the two very different values obtained through extrapolation of melting point versus crystallization temperature data has been resolved. It is demonstrated through studies of the melting point of polypropylene as a function of crystallization time that the dependence of melting point elevation on supercooling is the opposite of that of polyethylene. The thickening process is shown to be most effective at low supercoolings leading to abnormally high melting points for specimens crystallized at low supercoolings. The equilibrium melting point of isotactic polypropylene is close to 186°C . It is believed that the observed behavior is a direct result of polypropylene crystallizing in Regimes II and III, unlike bulk linear polyethylene which crystallizes in Regimes I and II. It is suggested that the behavior may be directly related to the length of continuous adjacent reentry folding generated under the different regimes.

The crystallization behavior of high molecular weight deuterated polypropylene has been studied using hot stage optical microscopy and differential scanning calorimetry. It is found that the equilibrium melting point is 8.3 to 8.9°C

below that of polypropylene, correlating well with a theoretical estimate of 8.7°C . The polymer shows a Regime II-Regime III transition, as does polypropylene, but the transition temperatures of both polymers are close to one another and unrelated to supercooling. It is suggested that this is a result of the Regime II - Regime III transition being controlled by molecular mobility factors, unlike a Regime I - Regime II transition temperature, which is controlled by supercooling. Values of fold surface free energy of deuterated polypropylene were found to approximately 60% of those of polypropylene.

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CHAPTER 1

INTRODUCTION

Polypropylene is a much studied polymer with several unusual features in its crystallization behavior, which have tended to make it more difficult to understand than polyethylene. There have always been two different values of the equilibrium melting point, T_m^0 , quoted in the literature. The extrapolated values of T_m^0 fall into two groups, one around 186°C and the other around 210°C [1-10]. Many earlier studies have been complicated by possible effects caused by a lack of close to complete isotacticity; modern polypropylenes are now better than 99% isotactic. Inconsistencies in extrapolated equilibrium melting points must be caused by differences in experimental approaches and errors in extrapolations, when care has been taken to choose a microstructurally pure polymer.

In estimations of the equilibrium melting point made using the experimentally determined relation between melting point and crystallization temperature errors can occur due to lamellar thickening. It has generally been recognized that lamellar thickening can occur at the crystallization temperature and during the heating necessary to obtain the melting curve [11,12]. There is a tendency for the "most accurately determined points," i.e., those produced at low supercoolings, to be high partly because of the long dwell

time needed at the crystallization temperature in order to crystallize a specimen. In turn this effect results in abnormally high values of the extrapolated equilibrium melting point. Conversely, it is also recognized that points obtained at high supercooling may in fact have been generated during cooling and be characteristic of a dynamic rather than an isothermal crystallization. They in turn tend to depress the value of the extrapolated equilibrium melting point.

It has generally been assumed that the thickening ratio (final to initial lamellar thickness) can be determined from the slope of the T_m versus T_c curve, following the schema of Hoffman and Weeks [13]. The crystals produced at high supercoolings are thinner and further away from equilibrium than those produced at low supercoolings. Therefore, their melting points are elevated by the thickening process much more than those crystallized at low supercoolings. In that approach thickening results in a lower slope to the plot, with the equilibrium melting point unchanged. In this thesis it will be demonstrated that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of the equilibrium melting point. The 210°C estimate of the equilibrium melting point of polypropylene is erroneous and caused by a relatively slow lamellar thickening process that occurs at the crystallization temperature.

Deuterated polypropylene is an isotactic polypropylene where all hydrogen atoms have been replaced by deuterium atoms. The aim of this study is to determine the influence of deuteration on crystallization and in particular on the regime transitions of polypropylene. The study includes analyses of the growth behavior of deuterated isotactic polypropylene, iPPD, using Avrami's analysis as well as a secondary nucleation analysis, and then to compare the results with a similar molecular weight of regular isotactic polypropylene, iPPH. In order to complete the analysis the equilibrium melting point of iPPD has been determined.

The effect of deuteration on the melting behavior of synthetic polymers has received some attention in the past [14-16]. Theoretical predictions tend to indicate that there should be a general depression of the melting point caused by the deuteration. Such predictions have been borne out in practice for polyethylene [17]. However, in the case of polypropylene the situation is not clear. What data are available suggest that no depression exists [14,15]. These reports were based simply on one experiment involving finite cooling rates and did not involve an estimation of the equilibrium melting point.

Both polymers have very high and similar molecular weights, about 257K. If there is any difference in equilibrium melting temperature, T_m^0 , between the two polymers

it could be compensated only by the C-D bond being slightly shorter than the C-H bond. As reported by Bates et al. [17], C-H and C-D bond lengths differ by 0.005 Å. The equilibrium melting point has been determined using the Hoffman Weeks approach [18] and it will be shown that there is a depression of the equilibrium melting point which correlates well with predicted values, within experimental error.

The kinetics analysis involve Avrami's equation [19,20] as well as secondary crystallization theory [21]. The Lauritzen-Hoffman theory [21] analyzes the growth data according to competition between the rate of deposition of secondary nuclei (i) and the rate of lateral surface spreading (g), resulting in three different regimes. Regime I occurs when $i \ll g$ and may be found at very low supercoolings; in regime II i is the order of g and occurs at moderate supercoolings; in regime III $i > g$ and is found at very high supercoolings. Regime behavior varies from polymer to polymer. For example cis-polyisoprene shows all regimes [22]; polyethylene when crystallized shows regime I and II [23,24]; whereas polypropylene shows regime II and III [4,9,24,25].

The influence of deuteration on regime transitions has not previously been studied and there are no *a priori* reasons for making a prediction. However, a Regime I-II transition would be expected to be very sensitive to the change in melting point that usually accompanies deuteration since the

transition temperature tends to be determined by supercooling. However it is by no means clear whether supercooling or mobility governs the Regime II-III transition, such as occurs in polypropylene and effects of deuteration will give valuable information on the nature of the transition.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Physical and Thermal Properties

2.1.1 Equilibrium Melting Temperature

In general, unlike other materials, a crystalline polymer does not exhibit a single melting temperature. To some extent it shows different melting points depending on its thermal history. It has been observed that the melting temperature of a polymer is directly related to its lamellar thickness. The thicker the lamellae are the higher the melting temperature. From this concept the equilibrium melting point is defined as the melting point of an infinitely large lamella. Theoretically the melting temperature (T_m) of a polymer is defined as follow:

$$T_m = T_m^0 - \frac{2\sigma_e T_m^0}{\ell \Delta H_f} \quad (2.1)$$

Where T_m^0 is the equilibrium melting temperature; σ_e is the fold surface energy; ℓ is the lamellar thickness; and ΔH_f is the heat of fusion.

However, in practice, the equilibrium melting point is mostly determined using Hoffman and Weeks approach [13,18], which is a plot of T_m versus T_c . The equilibrium melting point is the extrapolation to the line where $T_c = T_m$.

There have always been two different values of the equilibrium melting point quoted in the literature. Many earlier studies have been complicated by possible effects caused by a lack of close to complete isotacticity; modern polypropylenes are now better than 99% isotactic. Inconsistencies in extrapolated equilibrium melting points must be caused by differences in experimental approaches and errors in extrapolations, when care has been taken to choose a micro-structurally pure polymer.

The extrapolated values of the equilibrium melting point, T_m^0 , reported in the literature fall into two groups, one around 186°C and the other around 210°C [1-10]. Krigbaum^[1] and Miller^[2] have determined T_m^0 to be 186±2°C, whereas Fatou^[3] and Monnasse^[4] have extrapolated T_m^0 to 208°C. Samuels^[5] has found two different equilibrium melting points; one equal to 185°C and the other to 220°C. His work was based on different molecular orientations within semi-crystalline fibers.

Kamide and Yamaguchi^[11,26] have observed changes in melting temperature with crystallization time for different molecular weights and fractions of iPP. Their analyses were based on the shift of the peaks of the DSC plots. They noticed that at the same crystallization temperature the degree of shift is proportional to the crystallization time. Furthermore, as the crystallization temperature is increased, the degree of shift is progressively larger. At the end of their analysis they

concluded that the changes in melting temperature with time were independent of molecular weight and its distribution. But they did not study the effect of annealing on the equilibrium melting temperature.

In estimations of the equilibrium melting point made using the experimentally determined relation between melting point and crystallization temperature errors can occur due to lamellar thickening. It has generally been recognized that lamellar thickening can occur at the crystallization temperature and during the heating necessary to obtain the melting curve^[11,12]. There is a tendency for the "most accurately determined points," i.e., those produced at low supercoolings, to be high partly because of the long dwell time needed at the crystallization temperature in order to crystallize a specimen. In turn this effect results in abnormally high values of the extrapolated equilibrium melting point. Conversely, it is also recognized that points obtained at high supercooling may in fact have been generated during cooling and be characteristic of a dynamic rather than an isothermal crystallization. They in turn tend to depress the value of the extrapolated equilibrium melting point.

It has generally been assumed that the thickening ratio (final to initial lamellar thickness) can be determined from the slope of the T_m versus T_c curve, following the schema of Hoffman and Weeks^[13,18]. The crystals produced at high

supercoolings are thinner and further away from equilibrium than those produced at low supercoolings. Therefore, their melting points are elevated by the thickening process much more than those crystallized at low supercoolings. In that approach thickening results in a lower slope to the plot, with the equilibrium melting point unchanged. In this thesis it will be demonstrated that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of the equilibrium melting point. The 210°C estimate of the equilibrium melting point of polypropylene is erroneous and caused by a relatively slow lamellar thickening process that occurs at the crystallization temperature.

2.1.2 Glass Transition Temperature

The glass transition temperature, T_g , is the temperature at which the polymer undergoes the transformation from a rubber to a glass. Any material which can be cooled sufficiently below its melting temperature without crystallizing will undergo a glass transition. T_g is determined by measuring the specific volume of a polymer sample as a function of the temperature. The value of T_g depends on the cooling rate. Although the glass transition has the appearance of a thermodynamic second-order transition it cannot strictly be considered as one.

One of the most useful approaches to analyzing the glass transition is to use the concept of free volume. The free volume is the space in a solid or liquid sample which is not occupied by polymer molecules, i.e. the empty-space between molecules. It is envisaged that the free volume will be sensitive to the change in temperature. As the temperature of the melt is lowered the free volume will be reduced until eventually there will not be enough free volume to allow molecular rotation or translation to take place. The temperature at which this happens corresponds to T_g (Fig.2.1). The total sample therefore consists of volume occupied by molecules V_o and free volume V_f : $V = V_o + V_f$ and the fractional free volume, $f=V_f/V$: $f = f_g + (T-T_g)\alpha_f$ where α_f =thermal expansion coefficient of V_f and $f_g=V_f^*/V$.

Dependence of T_g upon chemical structure:

The most important factor is chain flexibility which is governed by the nature of the chemical groups which constitute the main chain. Polymer which have relatively flexible chains because of easy rotation about main chain bonds, tend to have low values of T_g . However, the incorporation of units which impede rotation and stiffen the chain clearly cause a large increase in T_g . The presence of side-groups on the main-chain has the effect of increasing T_g through a restriction of bond rotation. Large and bulky side-groups tend to cause the greatest stiffening and if the side-

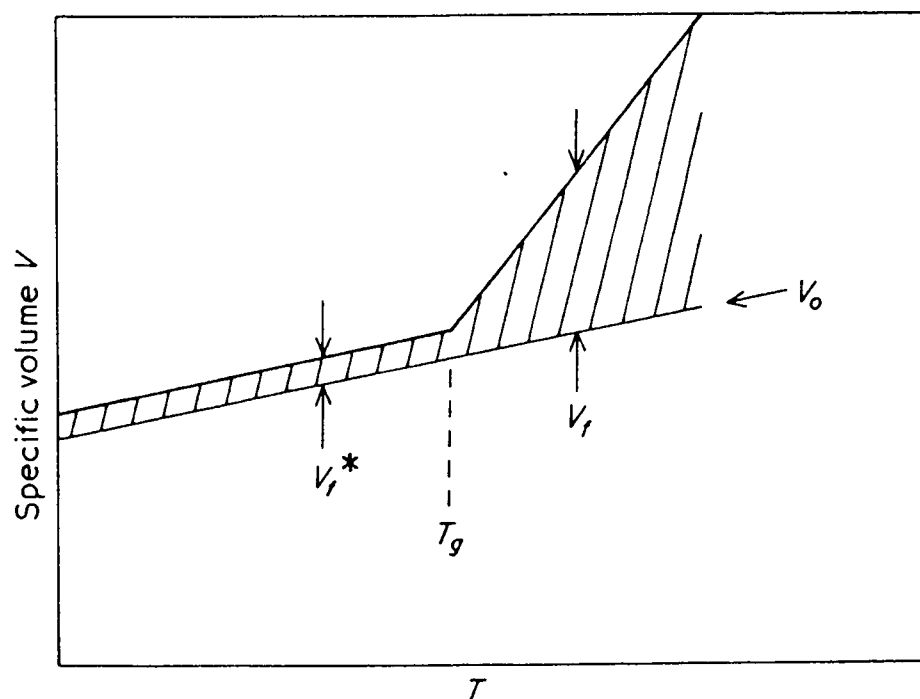


Fig.2.1: Schematic representation of the specific volume, V , of a polymer as a function of temperature, T . The free volume is represented by the shaded area.

group itself is flexible the effect is not so marked. The presence of polar groups such as $-Cl$, $-OH$ or $-CN$ tends to raise T_g more than non-polar groups of equivalent size.

In fact, the same factors tend to raise or lower both T_g and T_m as both are controlled principally by main-chain stiffness. It is found that when they are expressed in Kelvin the value of T_g is generally between 0.5 and 0.8 T_m .

2.2 Morphology of Isotactic Polypropylene

It had been confirmed during the late 1950s by Natta and Corradini [27-30] that the chain conformation of iPP is a three-fold (3_1) helix, which can be either right handed or left handed, with a periodicity of $6.50\text{\AA}$. The position of the methyl group (CH_3) with respect to the chain axis can be either up or down. As a consequence four possibilities, relative to a reference axis (Fig.2.2), can be determined for a three-fold helix of iPP in the crystalline state [27-33].

On the crystal lattice level, iPP exhibits three different morphological forms, α , β and γ , distinguished by the arrangement of the chains [34-40]. Each of these forms is identified with specific peaks in the x-ray pattern as shown in Fig.2.3. Another form of iPP having a degree of order intermediate between crystalline and amorphous phases was first reported by Natta [30], named the "smectic" form, and

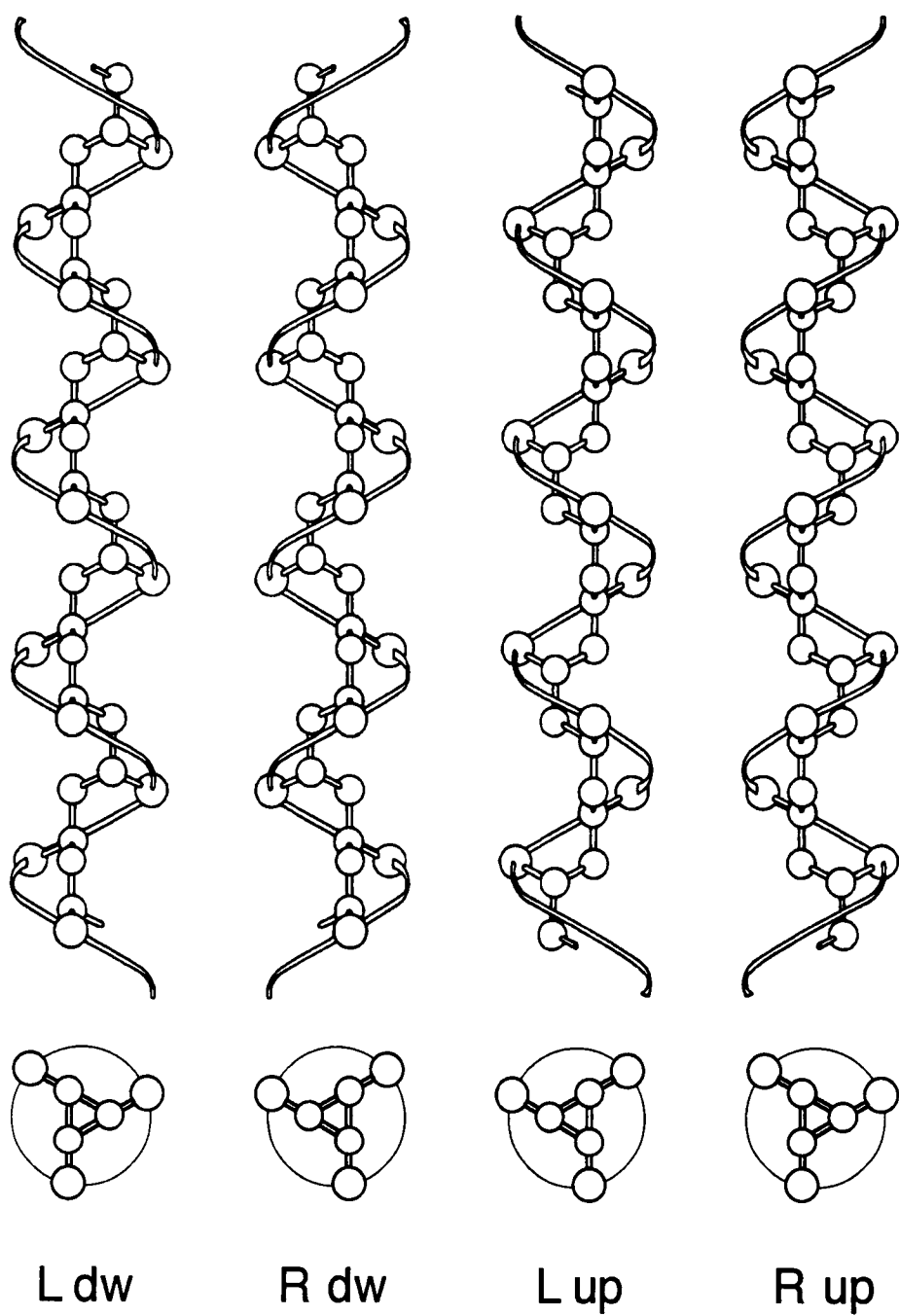


Fig.2.2: Chain configurations in isotactic polypropylene.

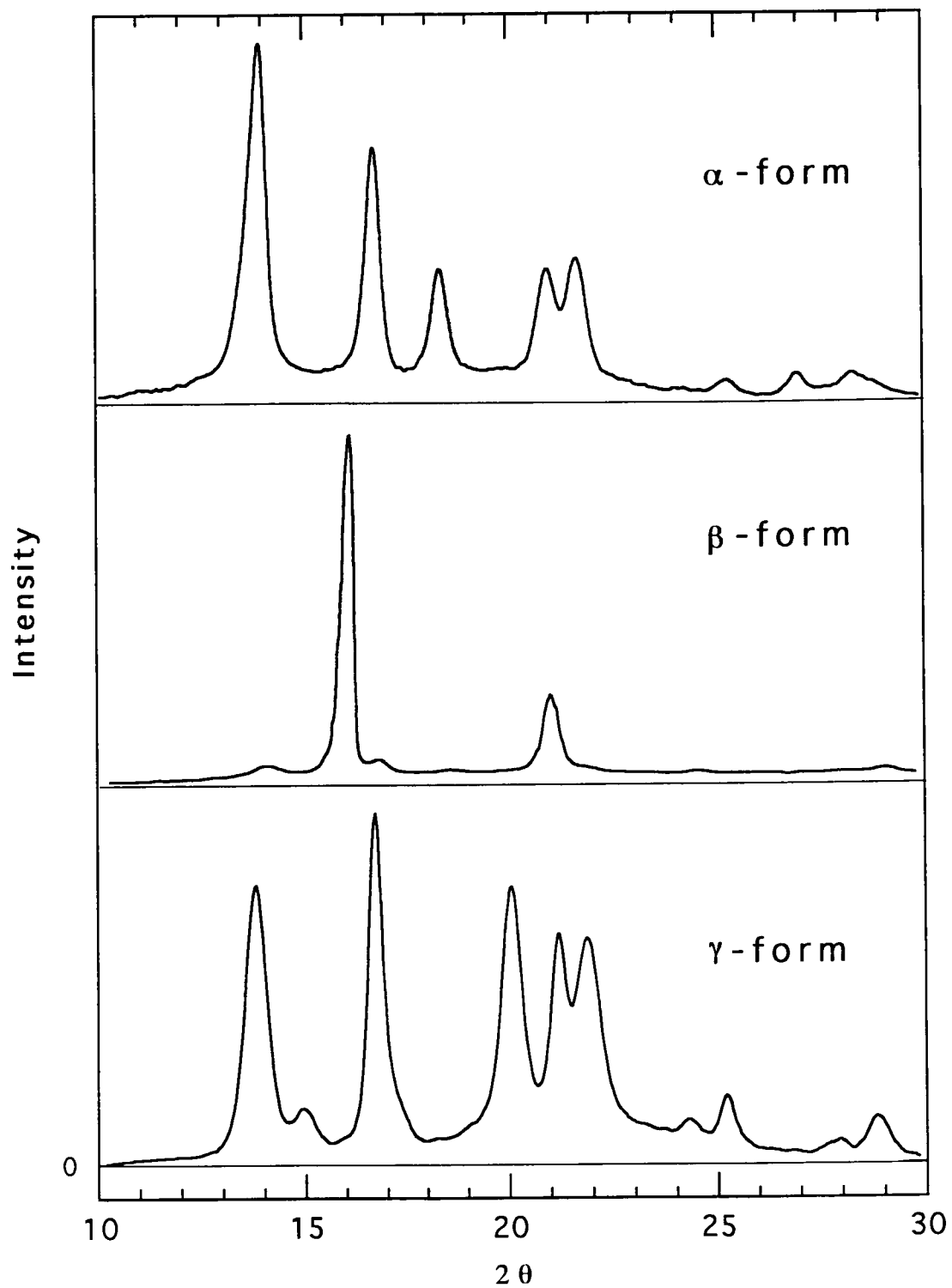


Fig.2.3: WAXD of different morphological forms.

has been described in some detail by Corradini and co-workers [41]. Each of these forms were observed with different preparation procedures [35,39,40].

It is well established that, when crystallized either from the melt or from dilute solution, iPP forms lamellar structures regardless of whether it is crystallized under quiescent or stress-induced conditions [37,42,43]. Lamellae are defined as ordered structures that contain polymer molecules in the form of platelets or ribbons, usually 20 to 500Å thick. It is believed that during crystallization polymer molecules fold back and forth on themselves to some degree to form lamellae. Usually, the radial growth of iPP lamellae is in the form of spherulites or discs [4,37,44,45]. In primary crystallization, the growing lamellae evolves from a nucleus through sheaf-like structures into the growing spherulite [37,43] (Fig.2.4). Growth continues until the spherulites come into contact with each other, i.e. impinge. The growth fronts of the spherulites finally result in a multitude of polygonal formations confined by straight or curved lines (Fig.2.5). Secondary crystallization occurs within the spherulite, transforming a portion of the interlamellar material into crystalline material.

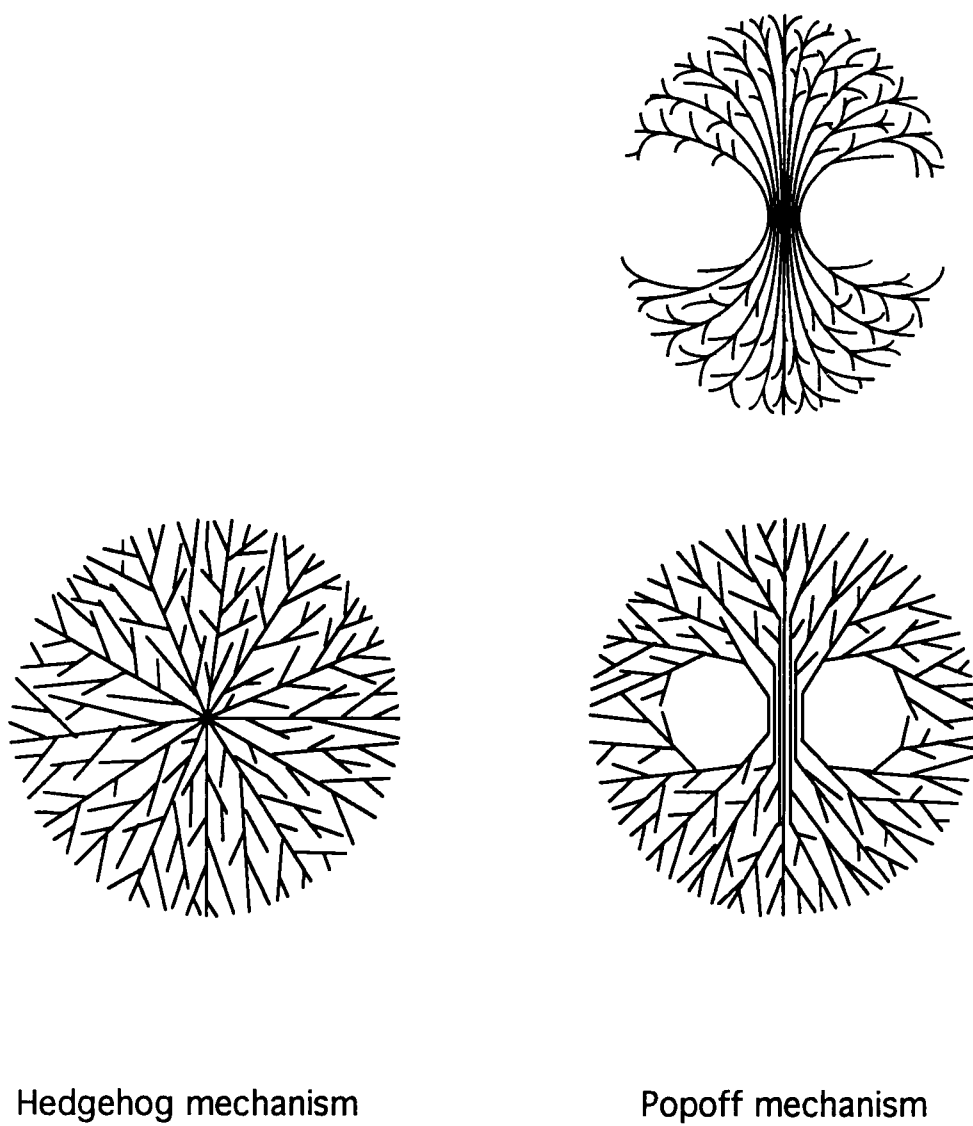


Fig.2.4 Schematic drawings of spherulite growth through repeated branching [141].

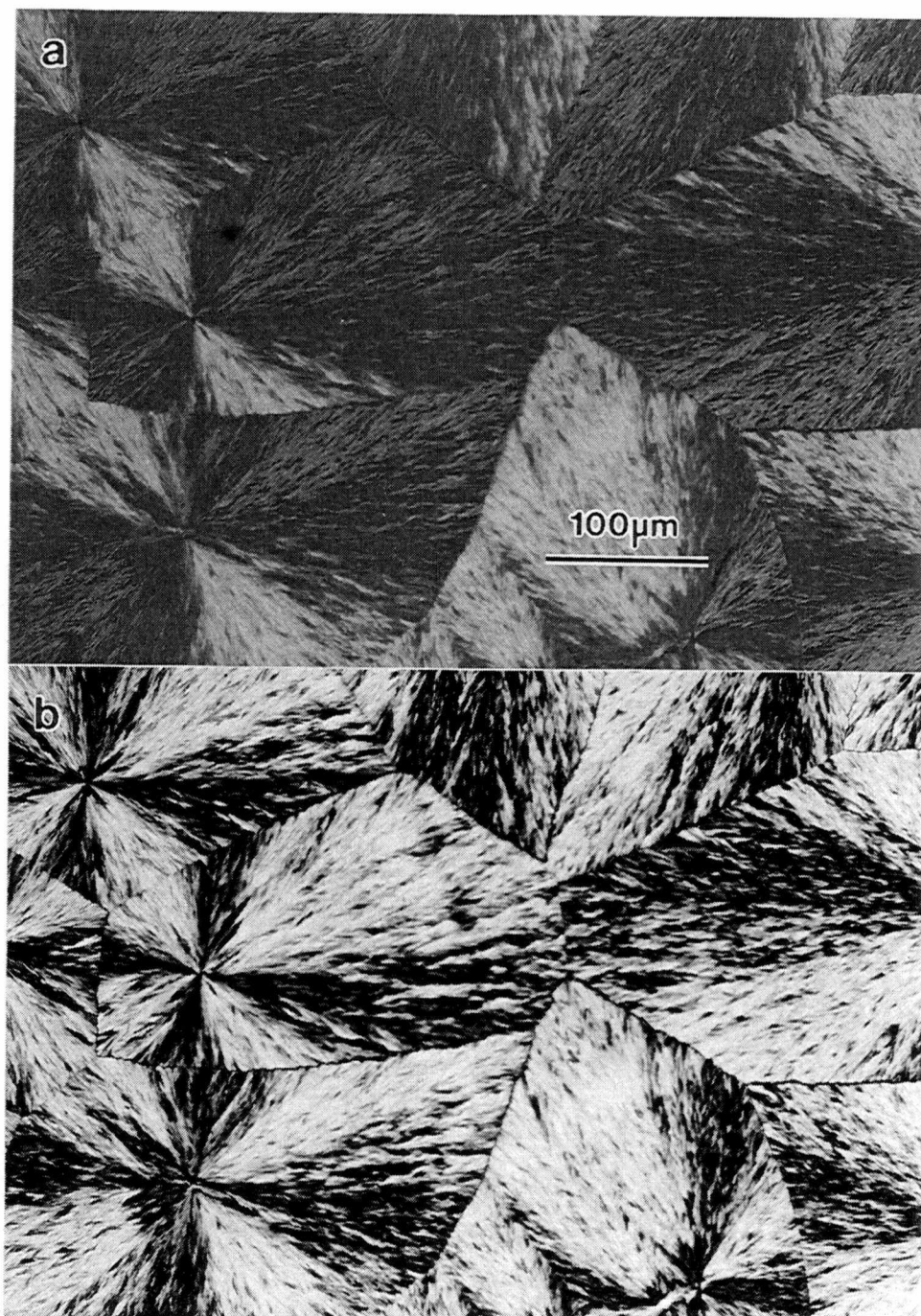


Fig.2.5 Impingement of spherulites. The contact between adjacent spherulites is either straight or curved lines. Top picture is taken using 1/4 wave plate under cross polar condition.

The complex arrangement of lamellae within a spherulite is also a unique morphological feature of iPP [37,42,44,46-48]. Under certain conditions, iPP has been shown to produce branches at an angle of 80° , as shown schematically in Fig.2.6 and optically in Fig.2.7. These branches are sometimes called 'cross-hatched' lamellae. The mechanism for the radial-tangential branching observed in iPP was explained by Lotz and Wittmann [47,48] as epitaxial growth of the tangential lamella on the radial one, due to crystallographic and structural interactions. These branching events may be so frequent, in certain instances, as to give rise to crystalline aggregates known as "quadrites", consisting of interwoven arrays of single crystal laths oriented at a fixed angle of 80° to one another [36,48-52]. In addition, 'cross-hatching' is also responsible for the peculiar optical properties observed in some iPP spherulites [39], as will be discussed later. Furthermore, iPP crystals have been known to induce epitaxial crystallization of a number of polymers with their chain axes tilted at large angles ($40-80^\circ$) relative to the helical axis direction present in the iPP substrate [47,50,51,53-57]. For example, epitaxial growth of polyethylene on iPP substrate or vice versa has been studied by many authors [47,48,53-57]. Homoepitaxy with an 80° tilt angle of iPP, where different chain axis directions coexist within the same lattice, was proposed by Brückner and Meille for the explanation of the γ -crystal structure [58,59].

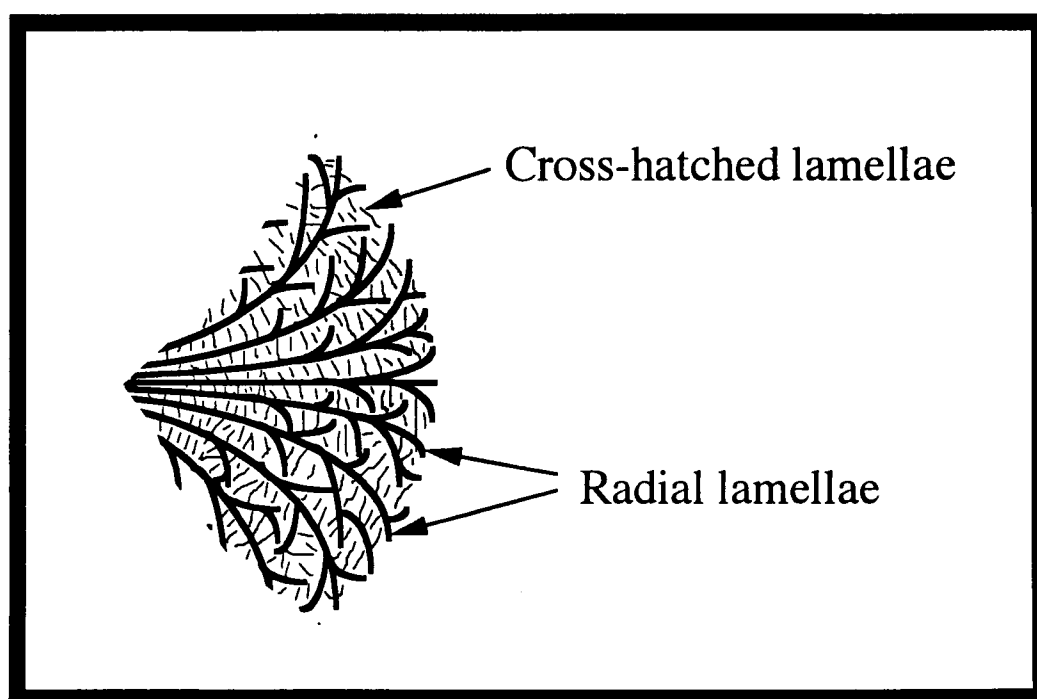


Fig.2.6 Schematic representation of branching and 'cross-hatching' in isotactic polypropylene.

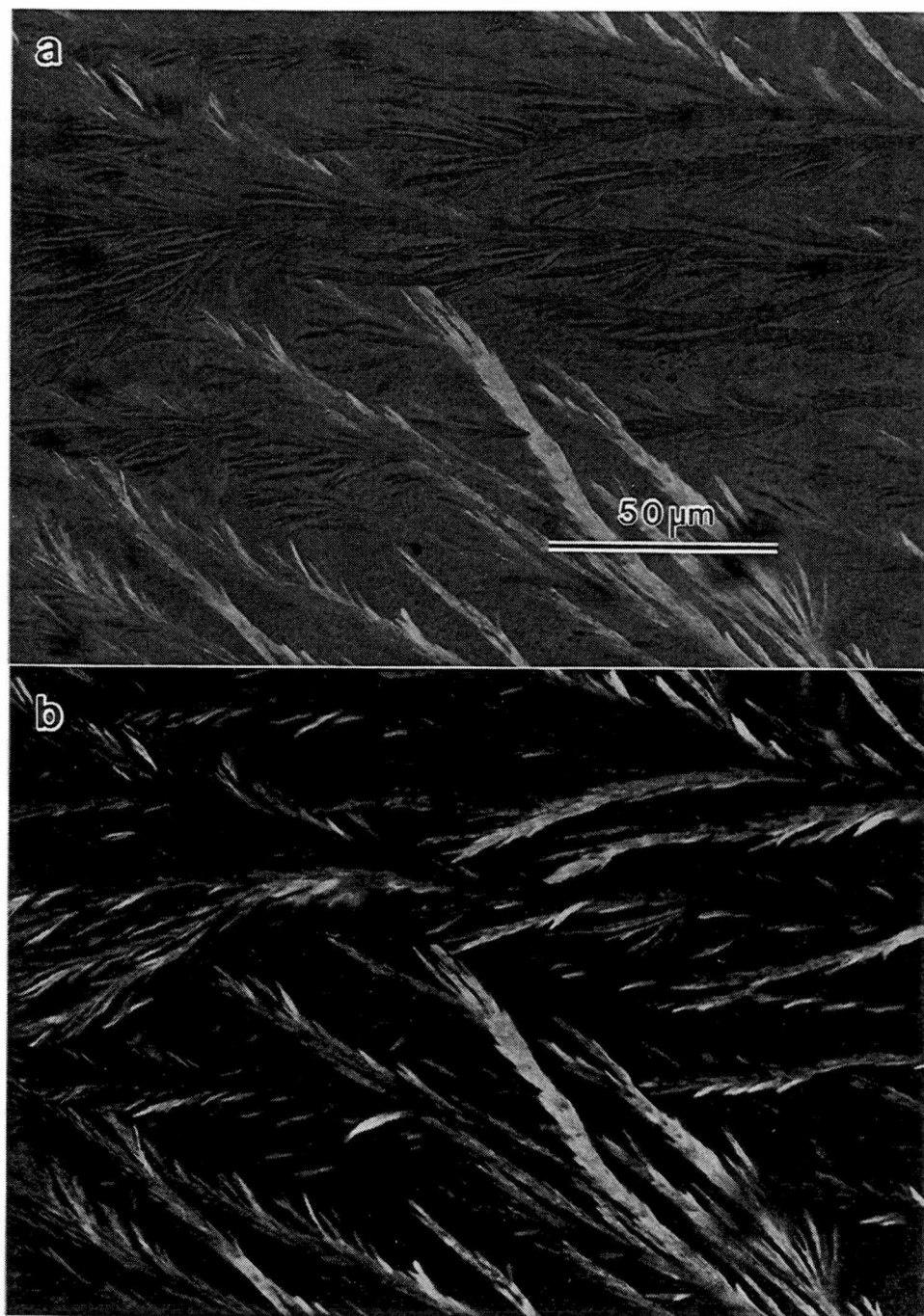


Fig.2.7 Optical observation of branching in α -iPP. a) With red filter (1/4 wave plate). b) Without red filter.

Using depolarizing light microscopy, several types of spherulite can be distinguished. Usually, 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 [60]. The birefringence of a spherulite, Δn , is defined as:

$$\Delta n = n_r - n_t \quad (2.2)$$

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 polar. When a spherulite is positive, its first and third quarter are blue (dark gray) and the second and fourth ones are yellow (bright gray) (Fig.2.8a), while a reversed arrangement of the quarters is observed for a negative spherulite [61] (Fig.2.8b).

Furthermore, depending on the feature of lamellae, the spherulites can be radial or ringed type. In radial spherulites, the lamellae are straight while, in the ringed ones, they are twisted around their longitudinal axes in a helical form [62]. Under a cross polarized medium, concentric dark rings appear corresponding to the pitch of the helix [40,44].

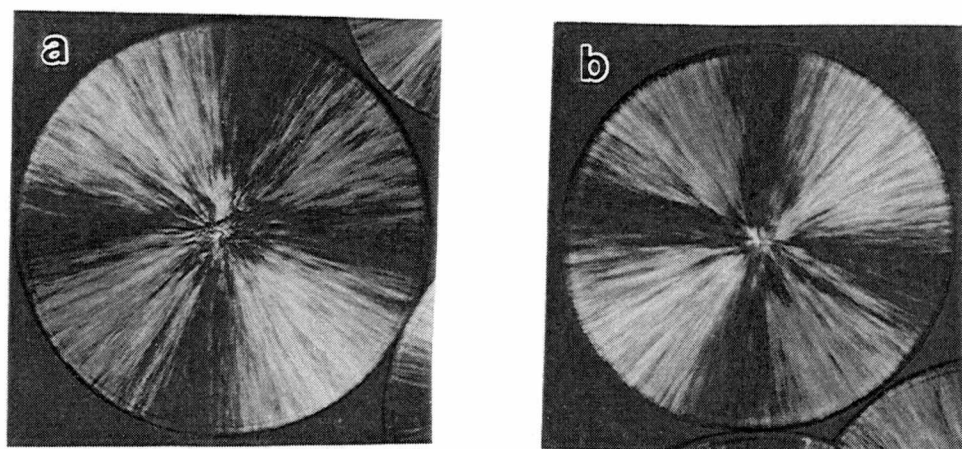


Fig.2.8 The sign of birefringence of spherulites:
a) Positive. b) Negative.

On the spherulitic level, iPP exhibits a variety of spherulite types 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 [44] in 1959. When iPP was crystallized in the temperature range 110-148°C, five distinct types of spherulites exhibiting different optical properties were identified as shown in Table 2.1. Among them three types exhibiting slightly positive, negative and mixed birefringence, revealed an x-ray diffraction pattern typical of the α -iPP crystal form. The other two types are less frequent and display negative birefringence, which belong to the β -iPP spherulites. 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 representing trends.

In the present review, essential results from x-ray and depolarized light microscopy of the supermolecular structure of iPP are discussed in four parts. The first three sections are concerned about the crystalline forms, namely α -, β -, and γ -form. The last part of the analysis will be devoted to the mesomorphic form, which is called "smectic".

Table 2.1: Classification of Polypropylene Spherulites according to Keith and Padden

Spherulite Type	I	Mixed	II	III	IV
Crystal Structure	α	α	α	β radial	β ringed
Sign of Birefringence	+ve	+ve	-ve	-ve	-ve
Crystallization Temperature ($^{\circ}\text{C}$)	<132	130-140	>138	<128	128-135

2.2.1 α -Form

The predominant crystal structure of pure (without nucleating agent) isotactic polypropylene, at atmospheric pressure, is the monoclinic α structure. In 1960, Natta and Corradini [30] calculated the unit cell parameters of the monoclinic α -iPP, which contains four three-fold helical chains, to be: $a = 6.65 \text{ \AA}$, $b = 20.96 \text{ \AA}$, and $c = 6.50 \text{ \AA}$, with $\alpha = \gamma = 90^\circ$, and $\beta = 99.3^\circ$. The space group has been assigned C2/c and Cc for the statistically ordered arrangement of up and down stems in the unit cell. Later, In 1972, Mencik [63] attempted to describe the crystal structure of α -iPP assuming space group P2₁/c for the random arrangement of up and down stems in the unit cell. Hikosaka and Seto [64] reinvestigated the crystal structure of α -iPP. As a result of their analyses and the ones of Mencik, the crystalline structure of α -iPP shows 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 crystalline structure of α -iPP by Petraccone et al. reveal several rules that govern the configurational characteristics of polymer stems [65,66]. However, the unit cell dimensions and the ordered arrangement of three-fold right- and left-handed helices within the cell remain substantially unchanged.

Different unit cell parameters were also given by Turner-Jones et al.^[35] for the monoclinic α -iPP as shown in Table 2.2.

The spherulitic morphology observed in melt crystallized iPP was first reported by Padden and Keith ^[44] who classified the spherulites with respect to their birefringence. The α -form of iPP exhibits three types of spherulites. Positive birefringence spherulites (α_I) can be developed at an isothermal crystallization temperature below 132°C (Fig.2.9). Negative birefringence spherulites (α_{II}) exist at a temperature greater than 138°C (Fig.2.10). 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 (Fig.2.11). 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 α -form spherulites has been directly related to the relative amounts of tangential lamellae, branching, inside the spherulites ^[36,37,43,67]. Norton and Keller ^[37] were able to prove that in the positively birefringent spherulites, α_I , the amount of branching lamellae is relatively higher than that of the negatively

Table 2.2 Lattice parameters of α -form iPP.

Bravais Lattice	Lattice Parameters ($\text{\AA}$)	No. Repeat Units	Density (g/cm^3)	References
Monoclinic	$a = 6.65$ $b = 20.96$ $c = 6.50$ $\beta = 99.3$ $\alpha = \gamma = 90^\circ$	12	0.938	29,30
	$a = 6.66$ $b = 20.78$ $c = 6.495$ $\beta = 99.62$ $\alpha = \gamma = 90^\circ$	12	0.946	35
	$a = 6.67$ $b = 20.94$ $c = 6.495$ $\beta = 99.62$ $\alpha = \gamma = 90^\circ$	12	0.937	35

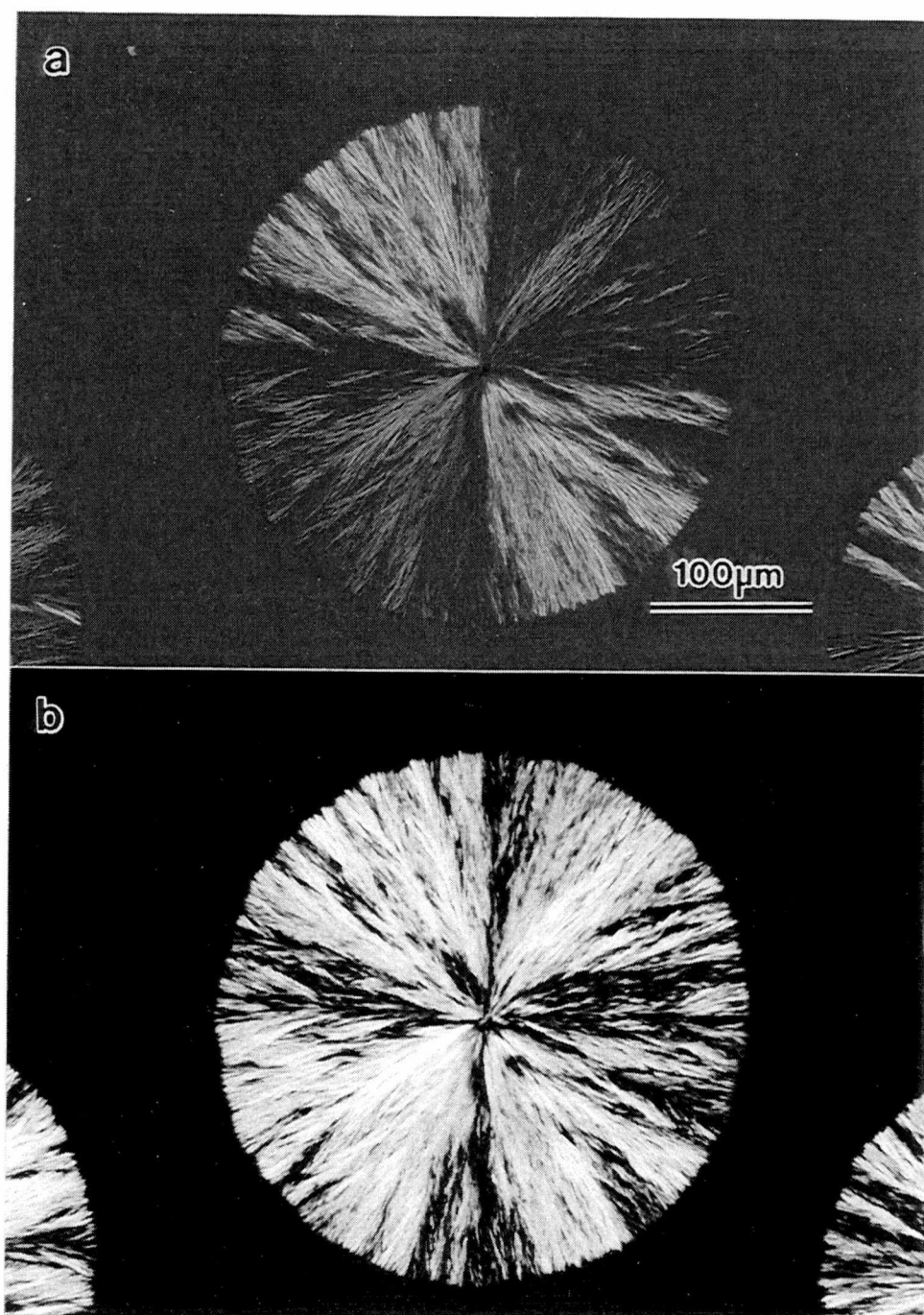


Fig.2.9 Positive birefringence spherulites, α_I , prepared at isothermal crystallization temperature of 115°C. a) With red filter (1/4 wave plate). b) Without red filter.

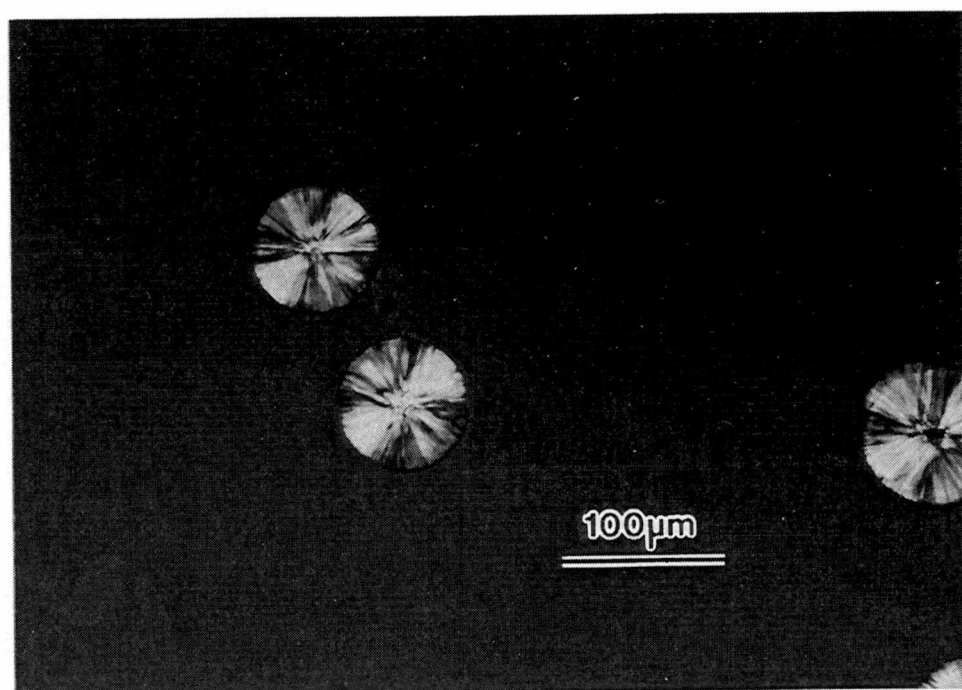


Fig.2.10 Negative birefringence spherulites, α_{II} , prepared at isothermal crystallization temperature of 140°C.

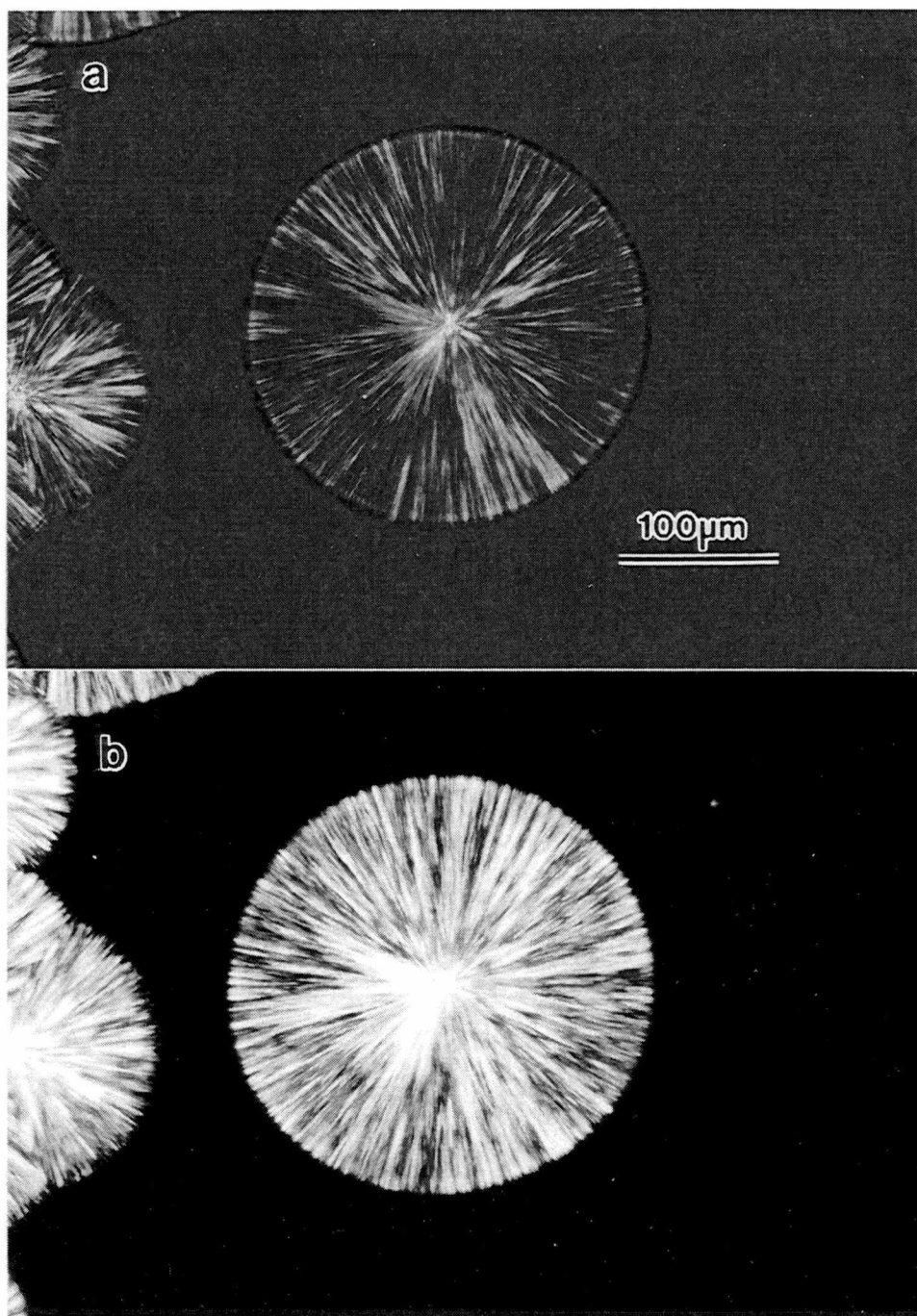


Fig.2.11 Mixed birefringence spherulites, α_m , prepared at isothermal crystallization temperature (T_c) of 120°C and 125°C. a) $T_c = 120$ with red filter. b) $T_c = 120$ without red filter.

birefringent α_{II} . It is well established that the proportion of the cross hatching phenomenon is reduced as the crystallization temperature increases until above 160°C, where only radially splaying lath-like lamellae develop. Thus for low crystallization temperature, below 132°C, spherulites have high tangential lamella content. Khoury [68] estimated the angle between branched lamellae, for twin crystals grown by crystallization in solution, to be $\approx 80^\circ$. This was in good agreement with electron microscopy results [36,37] and with other observations [46,48,49,69]. Important contributions in this field are also due to Padden and Keith [70].

The melting behavior of α -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 Fig.2.12. Consequently, during melting, a positive α_I - or a mixed α_m -spherulite becomes negative as demonstrated in Fig.2.13 and Fig.2.12c 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 (Fig.2.12).

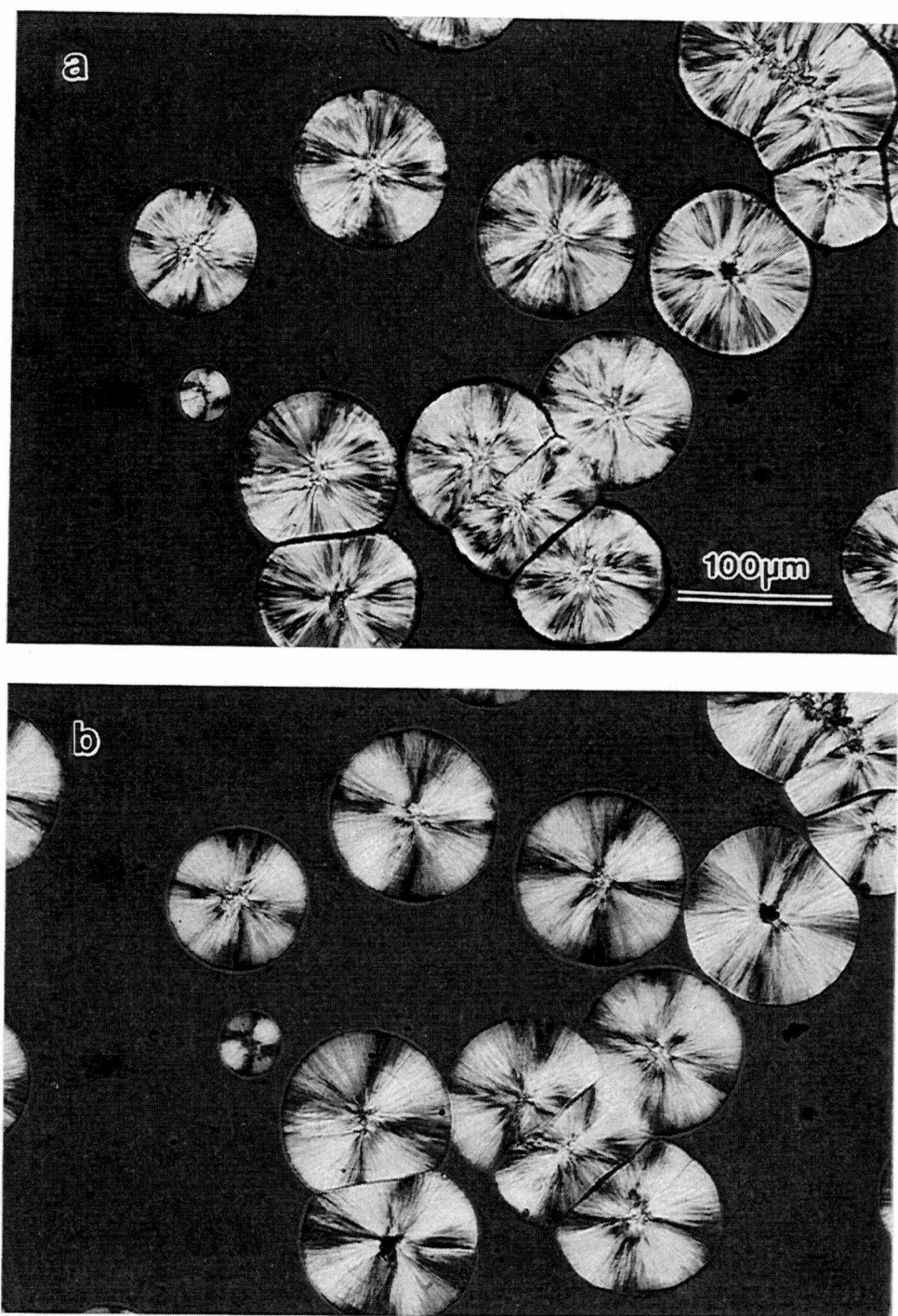


Fig.2.12 Melting of Mixed birefringence spherulites, α_m ,
During melting the sign of birefringence become
negative.
a) Crystallized at $T_c = 145^\circ\text{C}$.
b) $T = 166^\circ\text{C}$.

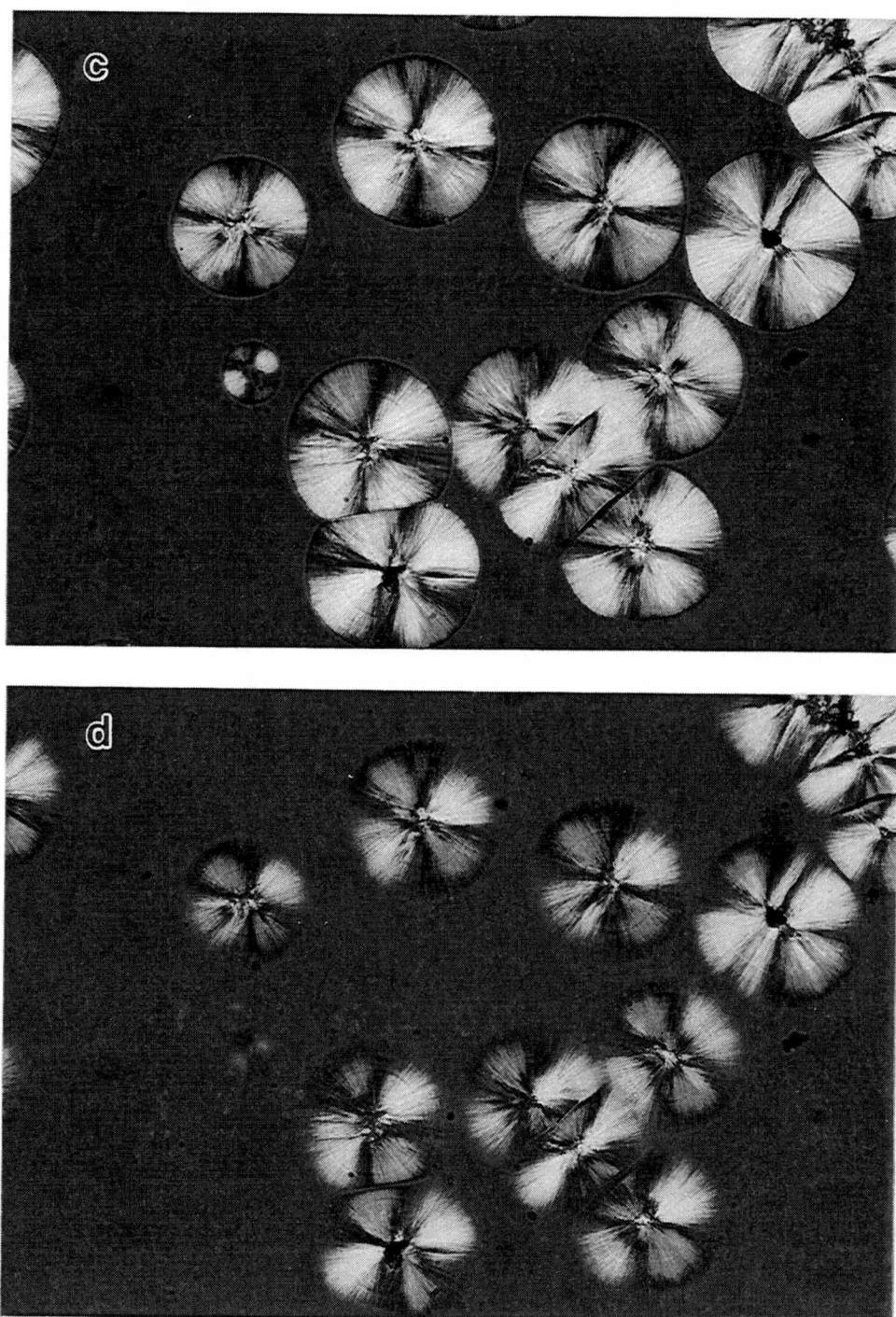


Fig.2.12 (continued) During melting.
c) $T = 168^{\circ}\text{C}$.
d) $T = 172^{\circ}\text{C}$.

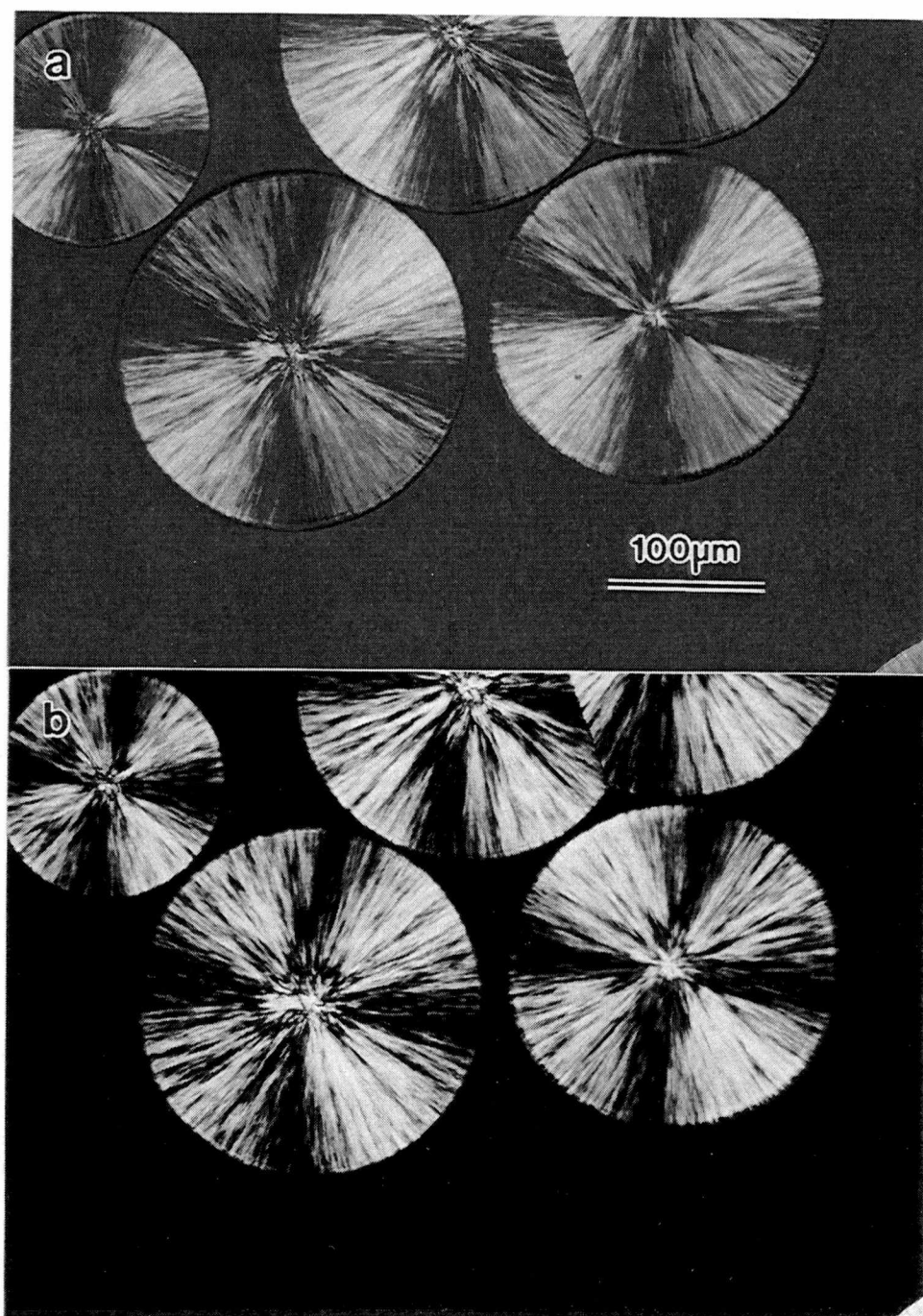


Fig.2.13 During melting positive birefringence spherulites, α_I , similar to the ones of Fig.2.9 become negative.

2.2.2 β -Form

The β -form of isotactic polypropylene, was first identified in 1959 by Keith et al. [71]. In the crystallization of conventional iPP grades, a small amount of β -form occurs sporadically at high supercoolings ($T_c < 130^\circ\text{C}$) or in quenched samples. However, under special crystallization conditions, when the temperature gradient method [72-74] is used or when selective β -nucleating agents are present [36,75-89], a high amount of β -form is produced. For example quinacridone dyes or triphenodithiazine are widely known β -nucleating agents to produce even 100% of the β -form under the appropriate thermal conditions of crystallization [86,88]. The same nucleants were also used to produce lamellar single crystals of the β -form, which were obtained either by melting and slow cooling iPP thin films, as reported by Geil [90,91], or by quenching a 5% iPP solution in paraffin wax from 210 to 100°C , as described by Turner-Jones and Cobbold [76].

The β -form is normally referred to as "hexagonal iPP", characterized mainly by two reflections at $d=5.53$ and $d=4.17\text{\AA}$. In addition to these two reflections, 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 as conversion to α -form take place on drawing. The derivation of the unit cell of the β -form of

unoriented specimens has been attempted by many authors as shown in Table 2.3. Keith et al. [71] suggested four-chain unit cell with $a=b=12.74\text{\AA}$ and $c=6.35\text{\AA}$. However, according to Addink and Beintema [34] this model implies excessively close methyl interactions ($3.6\text{\AA}$). Turner-Jones et al. [35,76] noticed that a considerable fraction of all the observed diffraction maxima can be accounted for by a hexagonal (or trigonal) lattice [34] with $a=b=6.36\text{\AA}$ and $c=6.49\text{\AA}$. Consequently, this cell can be recognized as the basic sub-cell of the β -structure. All the investigations in the more recent literature agree on this basic model. However, when additional reflections are taken into consideration, this model is not sufficient. A more satisfactory model is the hexagonal $P3_121$ with $a=b=11.03\text{\AA}$ and $c=6.49\text{\AA}$. Another possible unit cell, suggested by Turner-Jones and supported by Meille et al. [92], is the orthorhombic with $a=11.03\text{\AA}$, $b=19.10\text{\AA}$ and $c=6.49\text{\AA}$. The packing of the helical chains in the unit cell was suggested [35,76] to be unidirectional (left or right). The calculated density of the one chain hexagonal unit cell, is 0.92 g/cm^3 .

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 [44]. The first type is highly birefringent called

Table 2.3: Lattice parameters of β -form iPP.

Bravais Lattice	Lattice Parameters ($\text{\AA}$)	No. Repeat Units	Density (g/cm^3)	References
Hexagonal or Trigonal ($b = a$, $c = 6.49$, $\gamma = 120^\circ$, $\alpha = \beta = 90^\circ$)	$a = 6.36$	3	0.92	34
	$a = 11.01$	9		35
	$a = 12.72$	12		11
	$a = 19.08$	27		35
	$a = 22.03$	36		35
	$a = 25.43$	48		35
Orthorhombic	$a = 6.36$ $b = 11.01$ $c = 6.49$	6	0.92	11
	$a = 19.08$ $b = 11.01$ $c = 6.49$	18		35
	$a = 12.72$ $b = 22.03$ $c = 6.49$	24		35

negative radial, which grows below 128°C (Fig.2.14). The second type, negative ringed, is observed between 128 and 135°C (Fig.2.15). The temperature ranges for the formation of a particular type of spherulite have been reported differently, due to the variability in the characteristics of the molecular structure of iPP studied [37,93]. More detailed studies of the β -spherulites were accomplished by Samuels [5,94]. Accordingly, 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 the evidence discussed indicates that β -iPP lamellar crystals do not share either the peculiar lath-like shape or the branching morphology of α -iPP crystals.

Usually, the growth rate of the β -form exceeds that of the α -form, while its melting point is found to be in the 145-150°C interval, much lower than that of the α -form (Fig.2.16). Similar to the α -form, many values of the equilibrium melting point have been reported [74,81,88,94,95]; it varies between 170 and 200. Recently, Mezghani and Phillips reported the value of 174.4°C for T_m^0 of the β -form using the same procedure for determining the most accurate value T_m^0 of the α -form.

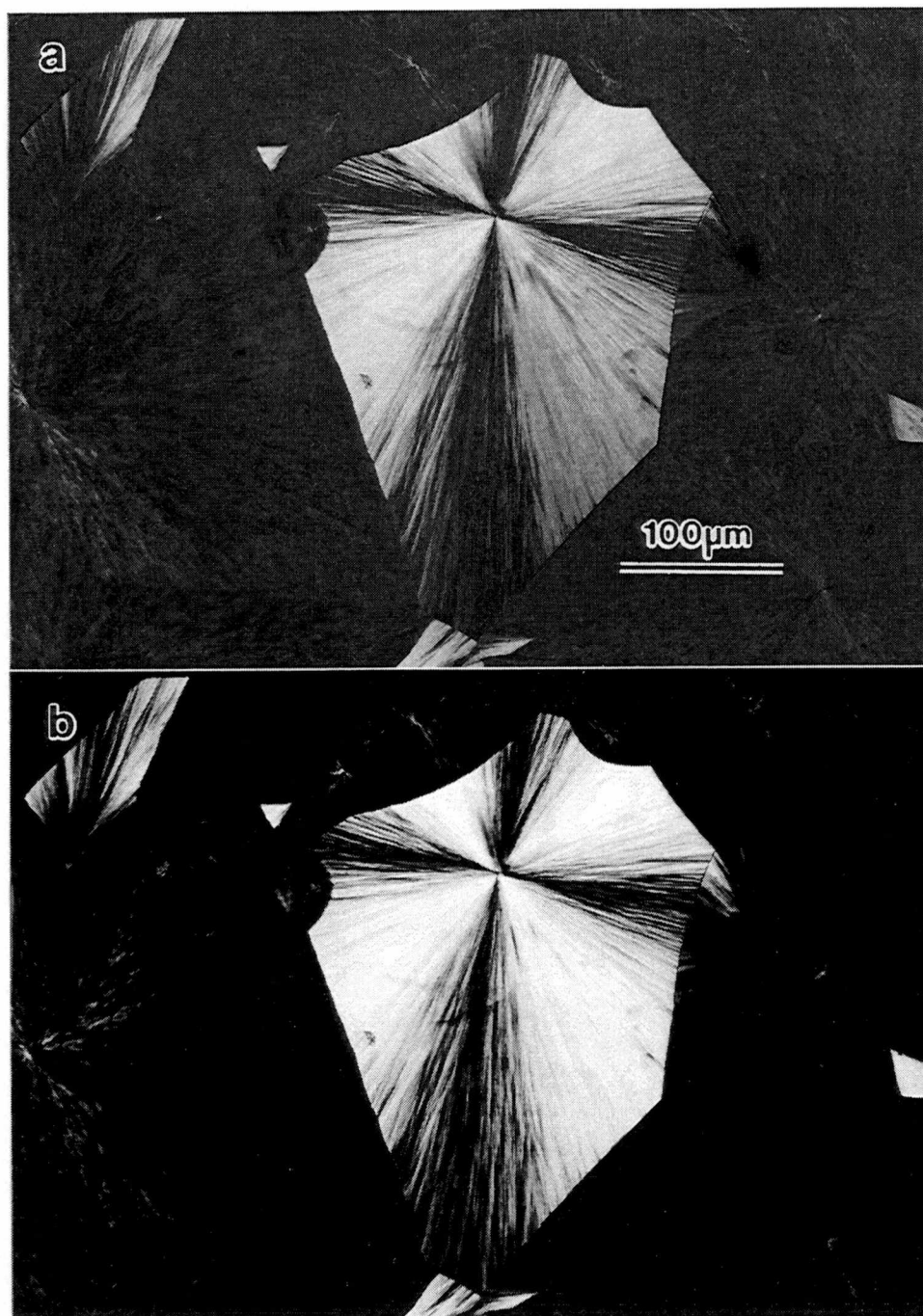


Fig.2.14 Negative radial β -spherulites surrounded by mixed type α -spherulites crystallized at 115°C. a) With red filter (1/4 wave plate). b) Without red filter.

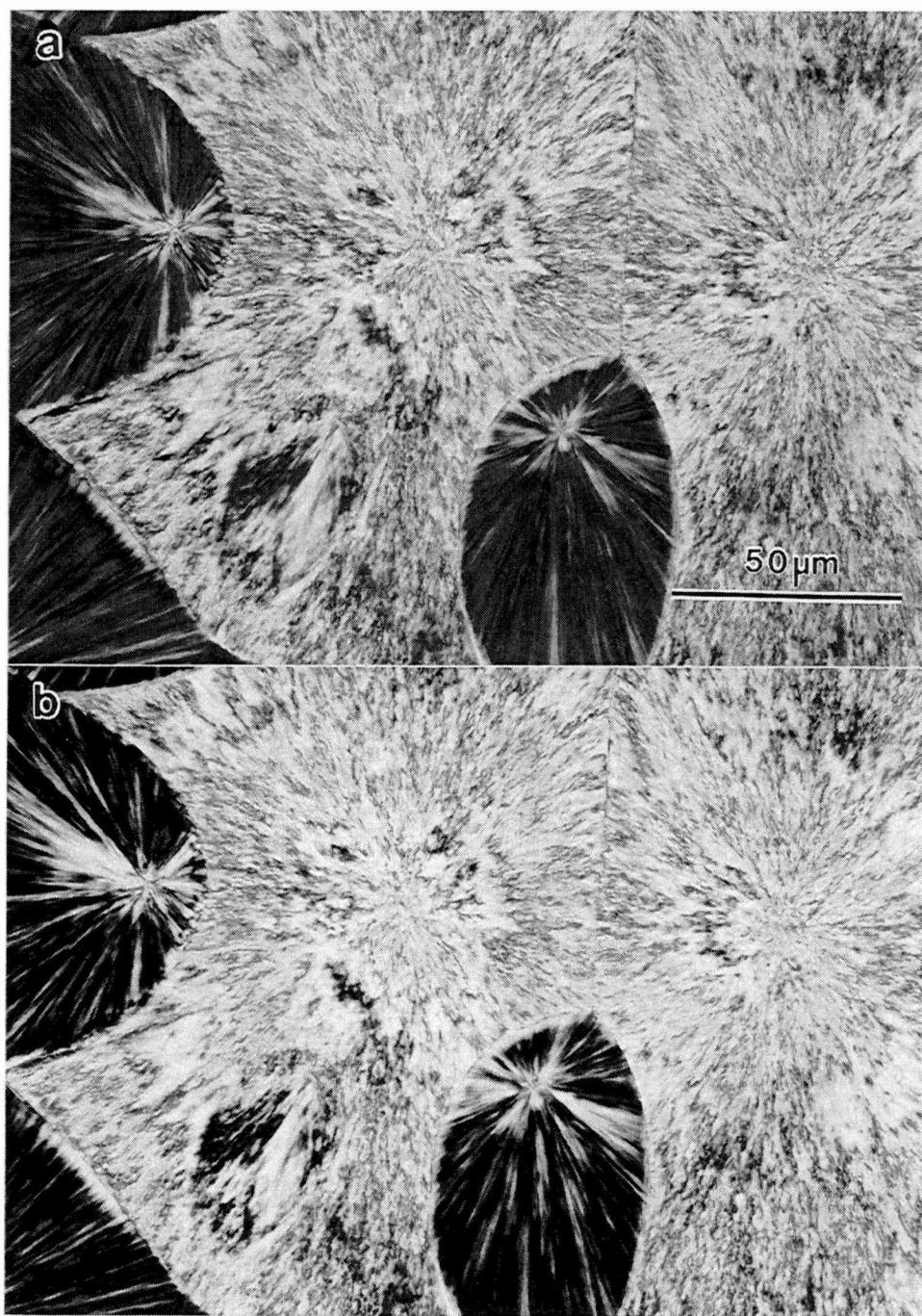


Fig.2.15 Negative ringed β -spherulites isothermally crystallized in 0.5% ethylene-propylene copolymer at 120°C.
a) With red filter (1/4 wave plate).
b) Without red filter.

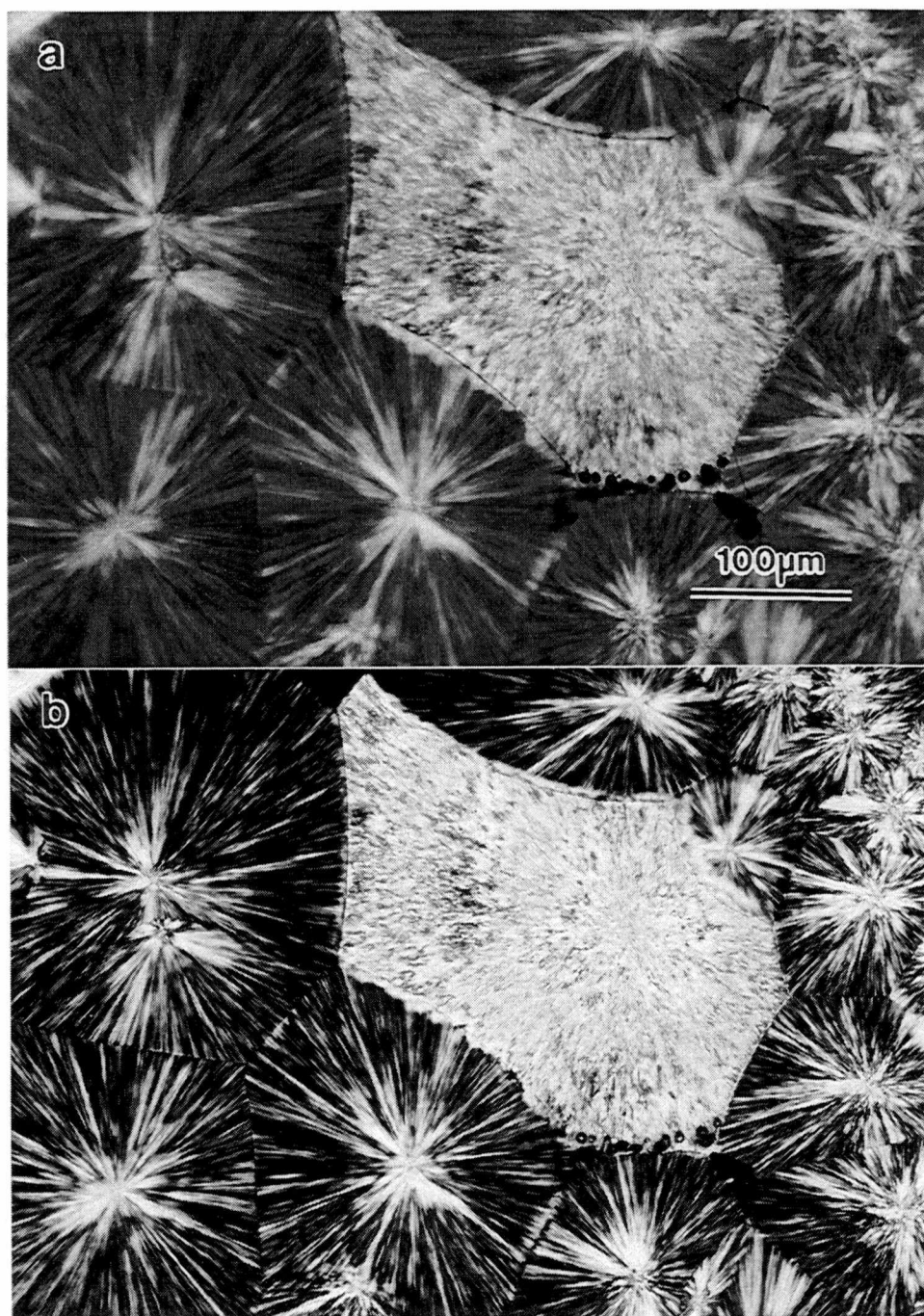


Fig.2.16 Morphological changes of the β -form during melting. The β -form melts first.

a) The β -form at $T_c = 120^\circ\text{C}$ surrounded by mixed type α -form. b) Same as the previous one without red filter. c), d), and e) During melting. f) Same as e without red filter.

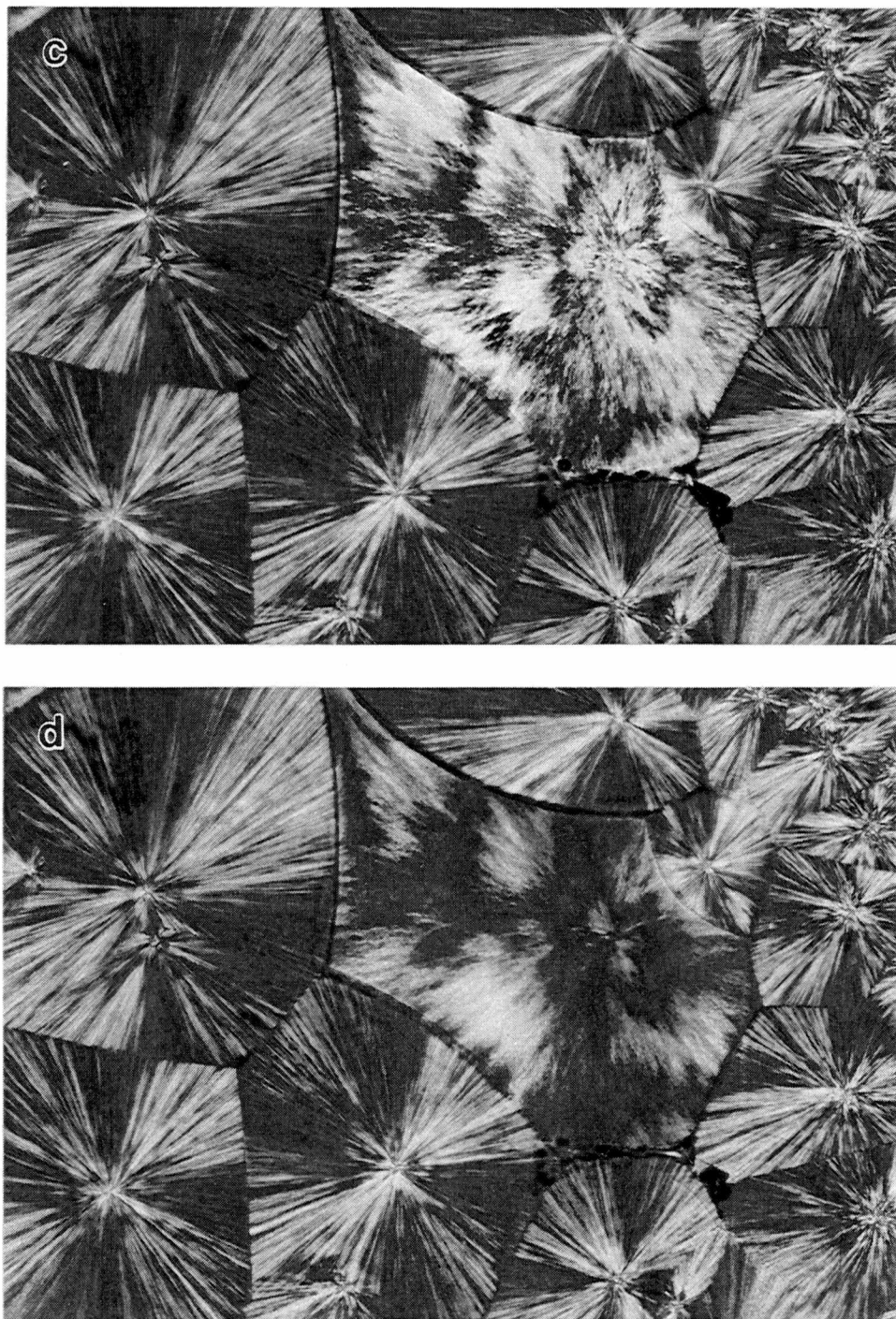


Fig.2.16 (continued) During melting.

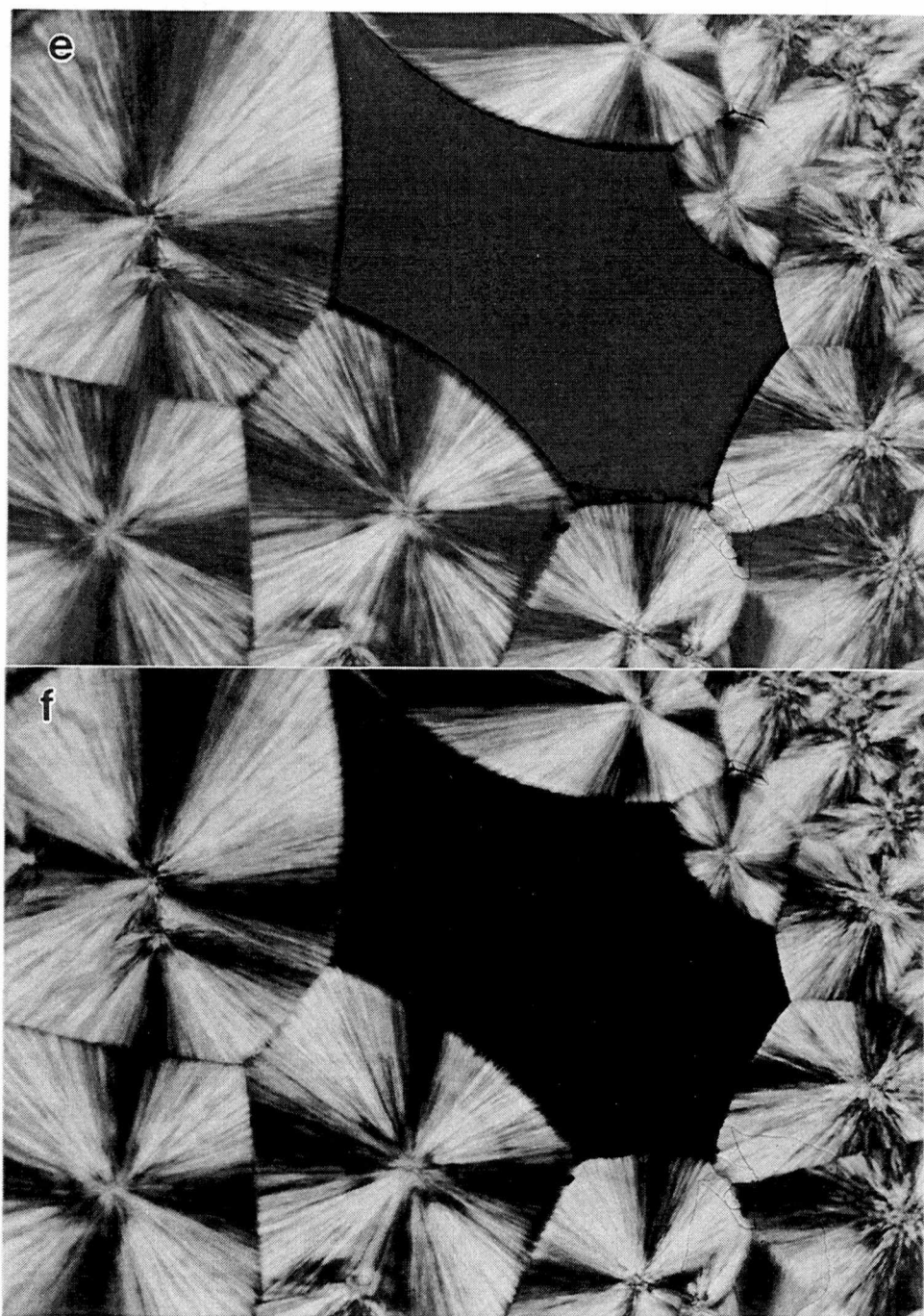


Fig.2.16 (continued) During melting.

The transition of the β -form to the α -form was also investigated by x-ray diffraction studies performed at different temperatures. According to Varga [40], when heating begins from the temperature of crystallization, the β -form does not recrystallize into the α -form. Instead, it melts separately as shown in Fig.2.16. 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. This critical temperature, T_R^* , is in the range of $\sim 100-110^\circ\text{C}$ [86-88]. 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, any 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. [96] using thermal analysis and optical and electron microscopy.

2.2.3 γ -Form

A number of general reviews have been devoted to this subject [34-36,77]. The γ -form of polypropylene was first noted during the 1960s [34,35,42,77,97-102] and was generated by several methods. 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 is crystallization from the melt of high molecular weight stereoblock copolymer with small amounts (3 to 10%) of ethylene or but-1-ene, showing to develop crystals of the γ -form. It appears therefore, that the presence of interruptions, rather than the specific nature of the interruptions, of isotacticity is the main feature promoting the γ -crystallization at atmospheric pressure.

Early studies had associated the formation of the γ -phase with chemical heterogeneity in the polypropylene chain caused by atacticity or by copolymerization [103]. More recent studies [104] have demonstrated that the γ -phase is produced at elevated pressures from high molecular weight homopolymers and that it 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. The analysis of Turner-Jones

[103] considered some copolymers of propylene with ethylene (as well as other comonomers) and found that the presence of a comonomer enhanced the formation of the γ -phase.

When varying the pressure only the α and γ forms are observed [97,104]. As the crystallization pressure increases the γ -form start to coexist with the α form until it becomes dominant at 2 kbar [104]. Furthermore, it appears from experiment that the lower the supercooling the higher is the amount of the γ -form produced at a specific pressure.

Similar to the β -form, all attempts to obtain oriented fibers of γ -phase produced only a transformation into the oriented α -crystals. Consequently, all the x-ray diffraction data available in the literature are either from powder or bulk samples. Though, diffraction patterns from γ -single crystals have been reported [105]. The γ -form was identified first as triclinic [98] with the unit cell being similar to that of the α form, with a slip along the c-axis direction ($a=6.54\text{\AA}$, $b=21.40\text{\AA}$, $c=6.50\text{\AA}$, $\alpha=89^\circ$, $\beta=99.6^\circ$, $\gamma=99^\circ$). Recent studies of a form generated at atmospheric pressure from low molecular weight iPP ($M_n=6300$) led to a reassignment of the structure as a face-centered orthorhombic unit cell with space group Fddd or Fdd2 [58,59]. The lattice parameters of the orthorhombic cell are: $a=8.54\text{\AA}$, $b=9.93\text{\AA}$, $c=42.41\text{\AA}$ (Table 2.4). The new structure accounts for the diffraction pattern in a more satisfying manner than the earlier structure.

Table 2.4: Lattice parameters of γ -form iPP.

Bravais Lattice	Lattice Parameters ($\text{\AA}$)	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	98
	$a = 6.55$ $b = 21.57$ $c = 6.55$ $\alpha = 97.4^\circ$ $\beta = 98.8^\circ$ $\gamma = 97.4^\circ$	12	0.935	58,59
Orthorhombic (Fddd, Fdd2)	$a = 8.54$ $b = 9.93$ $c = 42.41$	48	0.933	58,59,105

Figure 2.17 represents a schematic arrangement of chain stems in the γ -triclinic and the γ -orthorhombic unit cell. The new structure is unique, in that it contains sheets of parallel molecules, but the molecular orientation between adjacent sheets becomes non-parallel every two sheets. The angle between the non-parallel stems is about 81° .

On the spherulitic level, pure γ -form shows negative birefringence as shown in Fig.2.18. It is clear from Fig.2.19 that the lath-like structure of the α -form is absent in the γ -spherulites. However when α and γ -forms are present in the same sample the morphological features become complex. The optical studies of microtomed sections as reported by Campbell and Phillips [104] show no evidence of Maltese cross formation when less than 10% of the material is in the γ -form, whereas, when more than 60% γ -form is present, a clear Maltese cross exists. In addition, optical and electron microscope studies of etched specimens reveals no cross hatching in specimen with >60% γ -crystals. It should be pointed out that, the absence of branching in pure γ -form is also accounted for by the orthorhombic structure, since the process leading to branching in α -phase involves normal growth in γ -crystals.

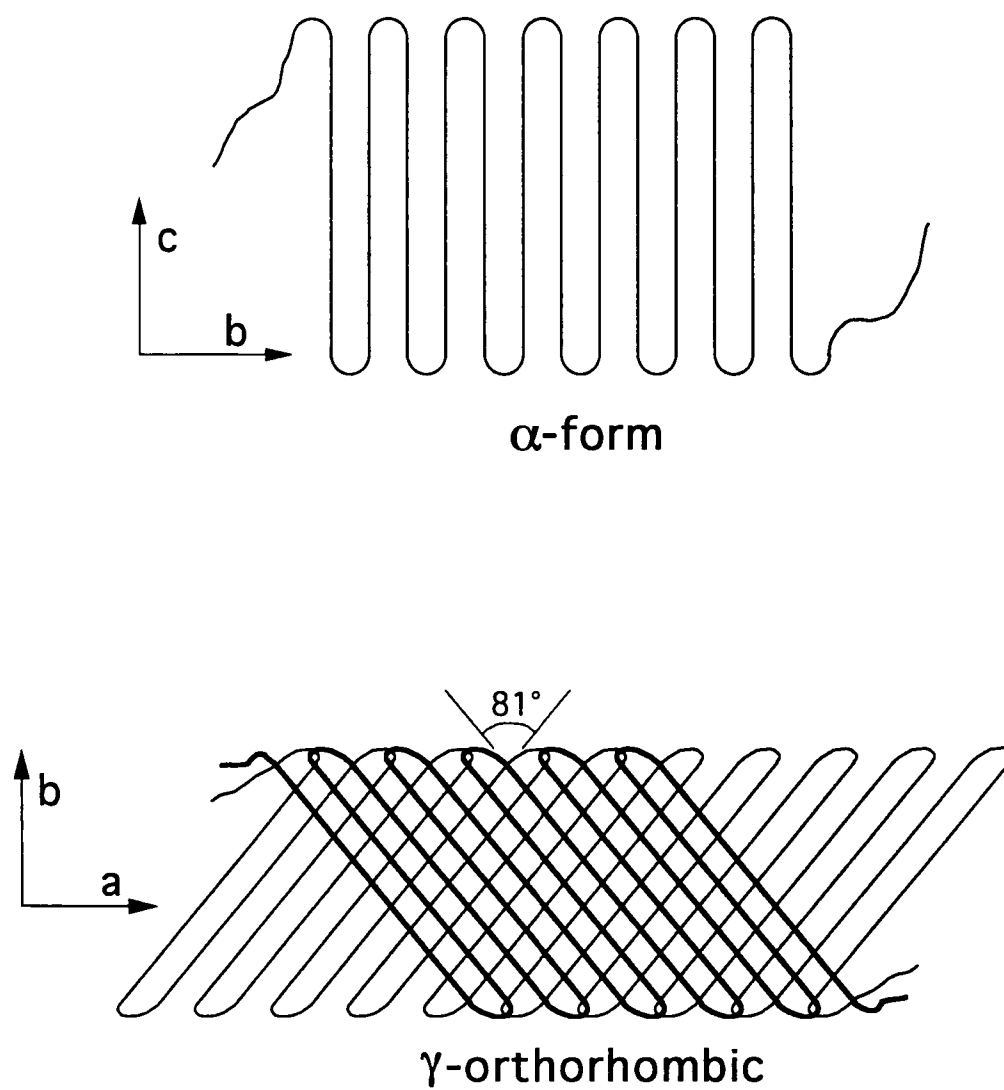


Fig.2.17 Schematic arrangement of chain stems in the α -monoclinic and the γ -orthorhombic unit cell.

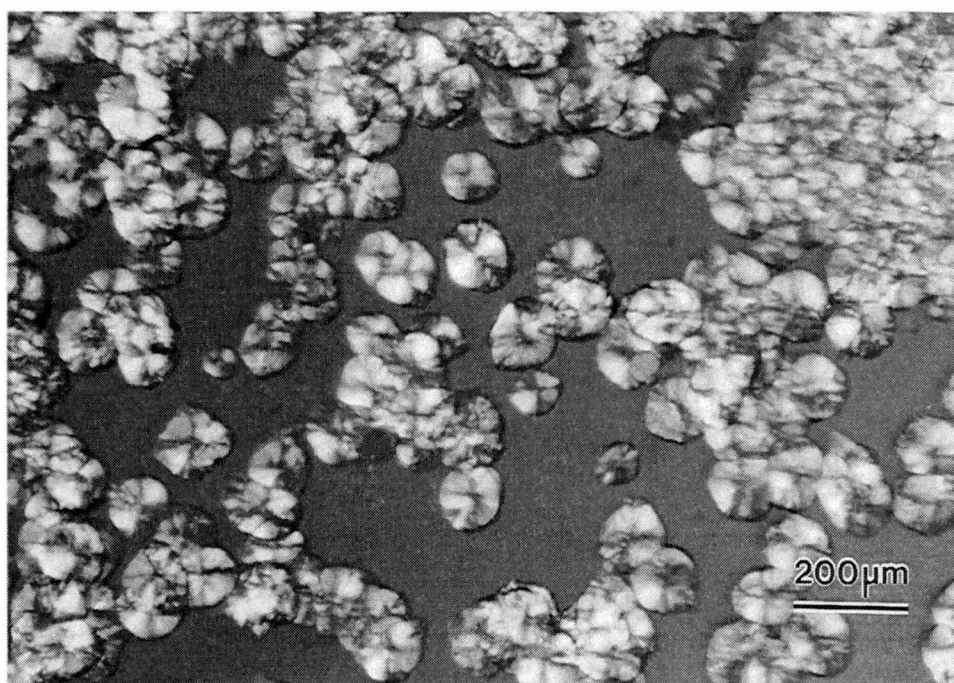


Fig.2.18 Spherulitic morphology of the γ -form. Sample is isothermally crystallized at 200 MPa (2 kbar) and 187.5°C. The spherulites show negative birefringence.

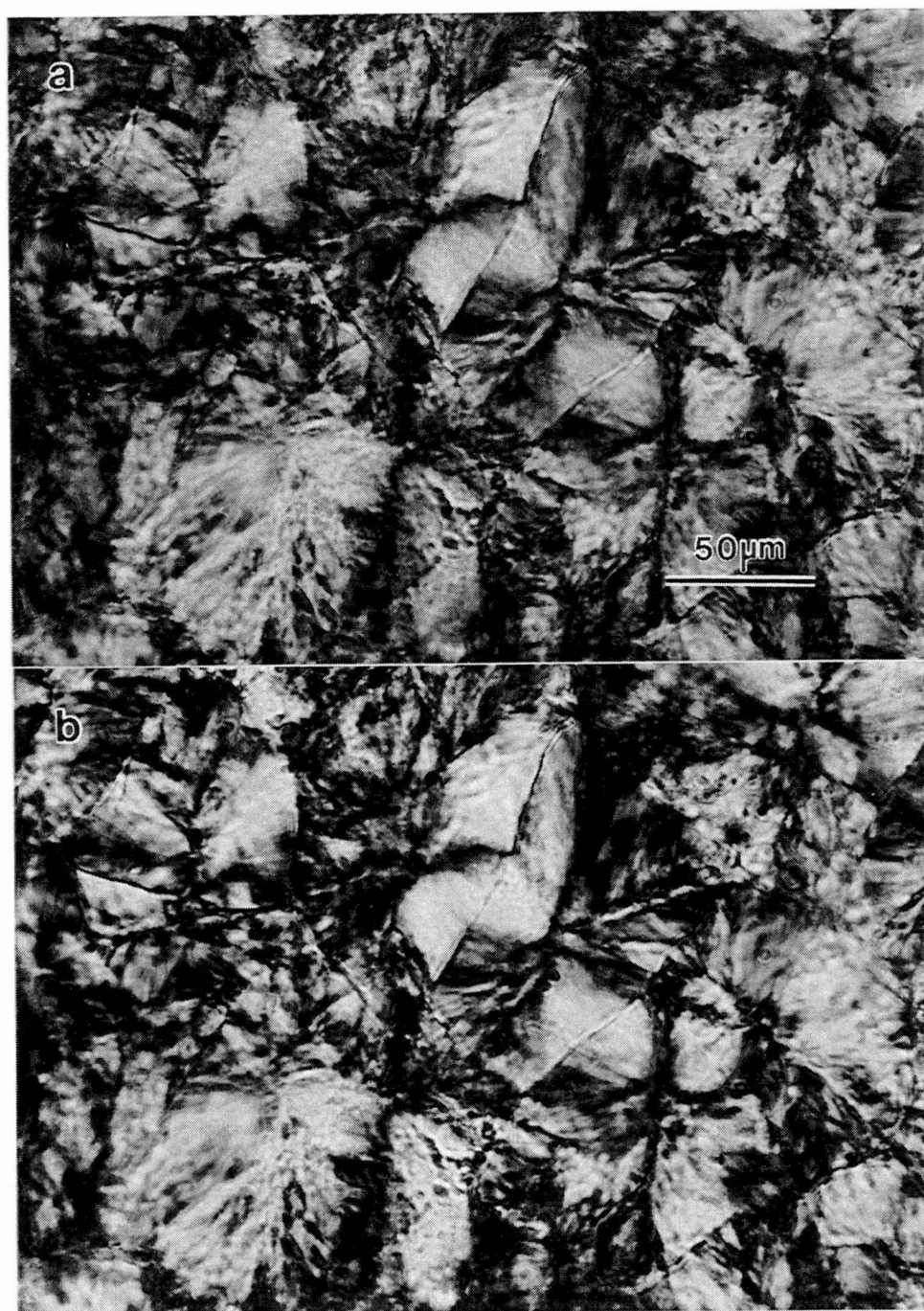


Fig.2.19 The γ -spherulites, which isothermally crystallized at 200 MPa (2 kbar) and 187.5°C, show no lath-like structure of the α -form. a) With red filter (1/4 wave plate). b) Without red filter.

The studies of Morrow and Newman [98], of low molecular weight ($M_n=1260$), show that solution crystallized iPP gives rise to needle-like crystals with the presence of both α - and γ -form structures. This morphology is also observed for high molecular weight samples crystallized at 125 MPa (1.25 kbar) where both the α -form coexist in small amount with the γ -form.

The contact faces of epitaxially crystallized γ - on α -substrates has been investigated by Stocker et al. [106] using electron microscopy and atomic force microscopy. 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 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.

2.2.4 Smectic

The smectic form is an intermediate crystalline order. This mesomorphic form was first named by Natta et al. [30] and later has been assigned different names. Miller [107] suggested that the order existing in this form might be of the type described in general terms by Hosemann [108] as

"paracrystalline". This term was also used by Zannetti et al. [109,110]. Wunderlich and Grebowicz [111] proposed the term "condis crystal", which means conformational disordered crystal.

The preparation of this form is very simple. It is obtainable by quenching thin sheets of iPP from the melt into ice water. The main characteristics of this mesomorphic form is indicated by two broad maxima x-ray diffraction, one at 14.8° and the other at 21.2° (2θ , $CuK\alpha$). The interpretation of the structure formed is still disputed in the literature [30,107,112-117]. Natta et al. [30] 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 lead Bodor et al. [113] to conclude that this form is composed of microcrystals of α -iPP. On the other hand, Gailey and Ralston [112] and later Corradini et al. [116] suggested that the smectic form contains small crystals of the β -iPP. This suggestion is based on the position of the two maxima of the smectic form being close to the position of the two most intense β -peaks.

The density of the smectic form has been reported by Natta et al. [30] to be 0.88 g/cm^3 , which is higher than that of atactic PP (0.85 g/cm^3).

2.3 Crystallization

Growth from a melt is extensively used for the preparation of crystals, for mass production as well as for the fabrication of high quality materials necessary for the modern technologies. It is then not surprising that nucleation and growth from the melt have been widely investigated from experimental and theoretical viewpoints.

For the growth of crystals, the interface between the two phases plays an important role since it is the region where the molecules are incorporated into the crystal lattice. This is particularly so in the case of growth from a melt where the molecules are always present at the interface. Transformation of liquid molecules into crystalline molecules is in this case essentially a local change in structure, associated with a small density change. The way in which these structural modifications occur is the growth mechanism, which is still not perfectly known for the crystal-melt system.

There are several methods for studying crystallization kinetics of polymers, which fall into two general categories: bulk or volumetric analysis, and crystal growth analysis. The simplest experimental study is the bulk growth, but it is the most difficult to analyze in detail. However, it can be analyzed partially using the Avrami equation [19,20].

2.3.1 Secondary Nucleation Theory

There have been many attempts to develop theories to explain the important aspects of crystallization [21,118]. The most widely accepted approach to the analysis of the linear crystal growth rates is the kinetic description due to Lauritzen and Hoffman [21].

The general expression of crystal growth as described by Lauritzen and Hoffman is:

$$G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp\left(-\frac{K_g}{T_c \Delta T f}\right) \quad (2.3)$$

where G is the growth rate, G_0 is the growth rate constant; U^* is the activation energy for polymer diffusion; R is the gas constant; T_c is the crystallization temperature (K); $T_\infty = T_g - 30$ (K); ΔT = supercooling, $(T_m^0 - T_c)$; f = correction factor, $\frac{2T_c}{T_c + T_m^0}$; K_g is the nucleation rate constant given by

$$K_g = \frac{j b_0 \sigma \sigma_e T_m^0}{k \Delta h_f} \quad (2.4)$$

where b_0 is the width of the chain, σ is the lateral surface free energy, σ_e is the fold surface free energy (Fig.2.20), T_m^0 is the equilibrium melting temperature (K), k = Boltzmann constant, and Δh_f is the heat of fusion. j is determined by the operating regime (see below) and is equal to 4 for regime I and III, and equal to 2 for regime II.

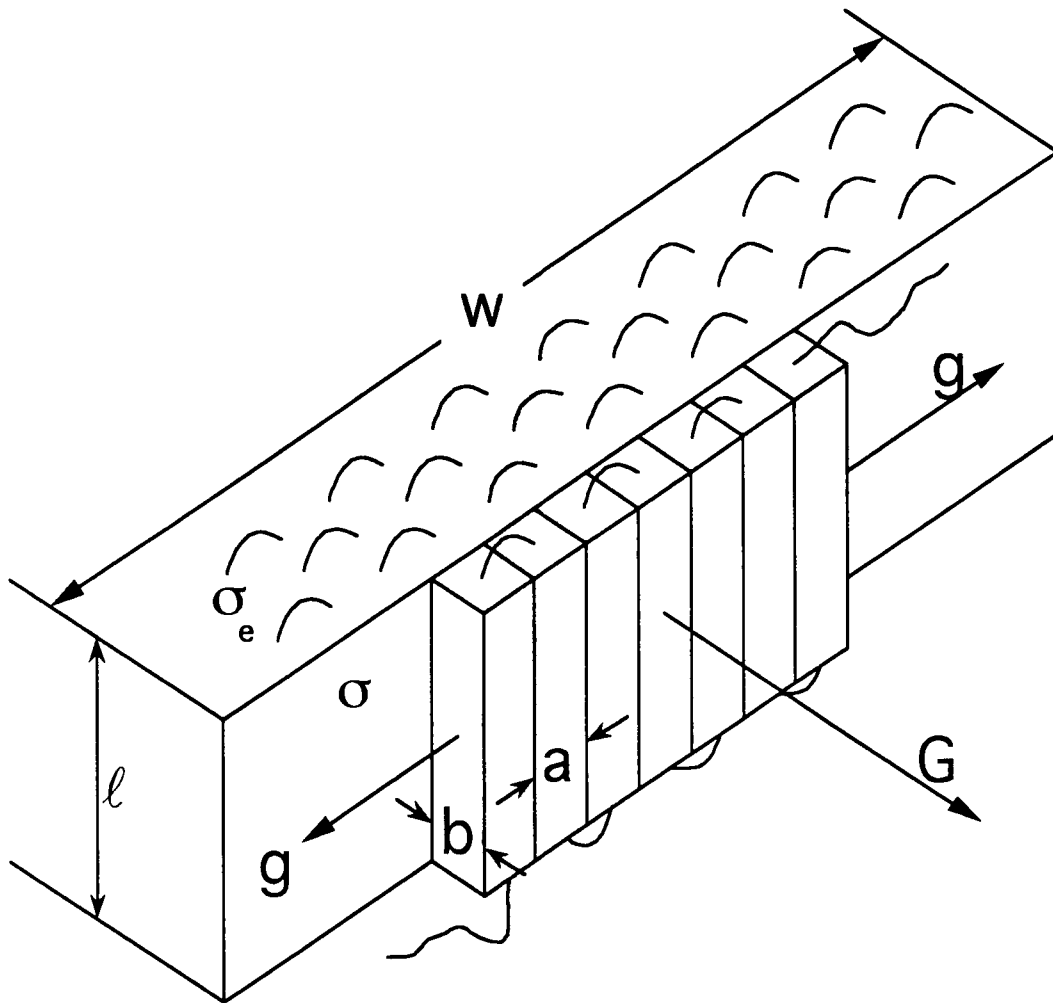


Fig.2.20 Schematic representation of an ideal lamellar growth front.

The Lauritzen-Hoffman theory analyzes the growth data according to competition between the rate of deposition of secondary nuclei (i) and the rate of lateral surface spreading (g) (Fig.2.20), resulting in three different regimes (Fig.2.21). Regime I occurs when $i \ll g$ and may be found at very low supercoolings; in regime II i is the order of g and occurs at moderate supercoolings; in regime III $i > g$ and is found at very high supercoolings.

Regime behavior varies from polymer to polymer. For example cis-polyisoprene shows all regimes [22], polyethylene when crystallized shows regime I and II [23,24], whereas polypropylene shows regime II and III [4,9,24,25]. Also the regimes depend on the conditions of crystallization, for example at atmospheric pressure high molecular weight polypropylene shows regime II and III; whereas the same material shows all regimes at 150 MPa [10].

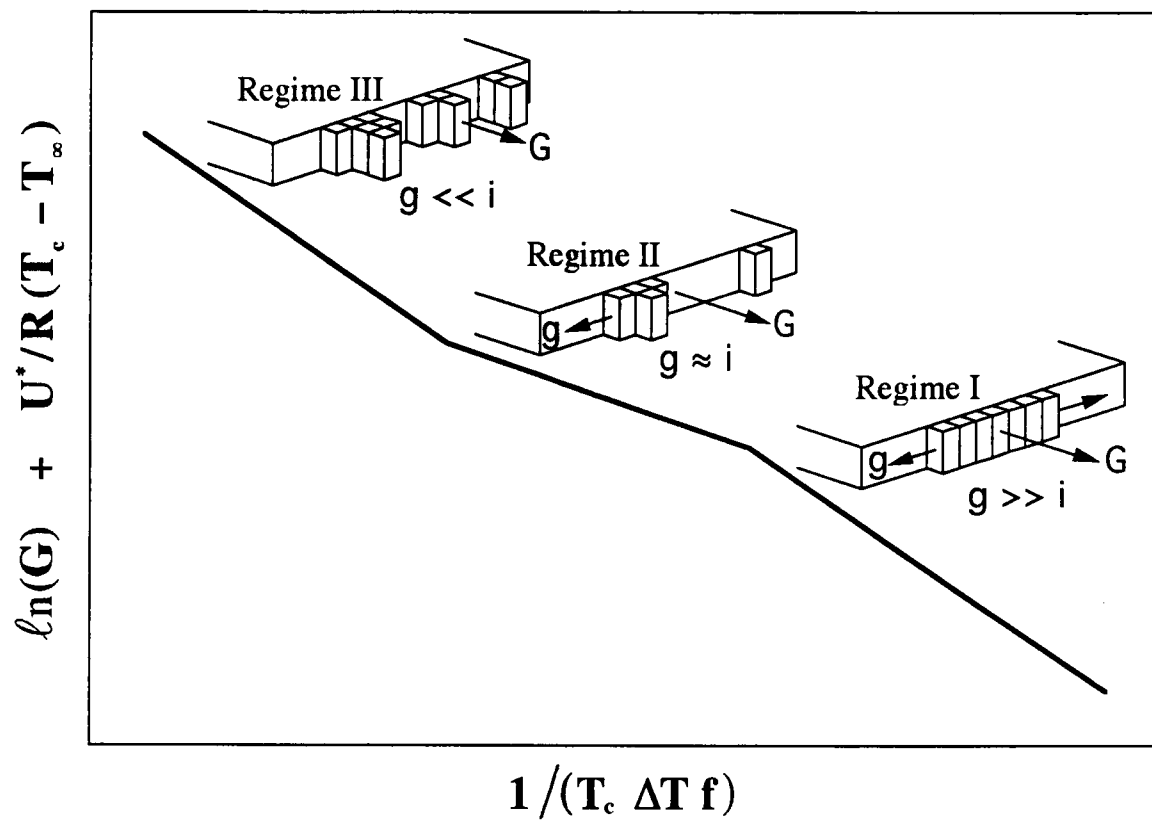


Fig.2.21 Schematic of regime analyses.

The Regime II-III transition is envisioned as the point at which the rate of surface spreading becomes less than the rate of secondary nucleation. Surface spreading, for an adjacent reentry system, is essentially a reeling-in process dependent on the reptational ability of the polymer chain.

The slopes of the secondary nucleation plots can be used to estimate the fold surface free energies of the two polymers. In order for these calculations to be carried out it is necessary to have estimates of the parameters which appear within equation 2.4. The equilibrium melting point has to be determined in separate experimentation.

The values of $\sigma\sigma_e$ can be determined from the slope of the lines. In order to proceed further it is necessary to estimate σ independently. One way to do this is to use the Hoffman modification of the Thomas-Stavely relation ^[119].

$$\sigma = 0.1 \Delta h_f \sqrt{a_o b_o} \quad (2.5)$$

The work done by the chain (q) to form a fold can be easily calculated from the following equation, when the fold surface energy is known.

$$q = 2 a_o b_o \sigma_e \quad (2.6)$$

Effects of T_m^0 , T_g , and U^*

In order to evaluate the effect of different parameters on the analysis, an ideal growth system is generated from equation 2.3 using the following variables: $T_m^0 = 186.1^\circ\text{C}$; $T_g = -12^\circ\text{C}$; $U^* = 1500\text{cal/mol}$; $\sigma = 10\text{ erg/cm}^2$; $\sigma_e = 100\text{ erg/cm}^2$; $\Delta H_f = 209\text{ J/g}$. Plot of growth rate versus temperature for this ideal polymer which has three regimes can be seen in Fig.2.22. When the data are analyzed using the Lauritzen-Hoffman equation, Fig.2.23, it is seen that this polymer shows the Regime I- Regime II and Regime II- Regime III transitions at 150 and 135°C , respectively.

The effects of different values of the thermodynamic variables on the analyses and on the regime transition temperature have been explored. Figure 2.24 and Table 2.5 show the effect of T_m^0 . In this analysis the values of T_m^0 used are 176.1°C , 186.1°C , and 196.1°C . Variation in T_m^0 has the greatest effect on the shape of the secondary nucleation plot, but does not significantly alter the regime transition temperature. Changes of the values of U^* (Fig.2.25) and T_g (Fig.2.26) simply causes the curve to move up or down without changing its shape.

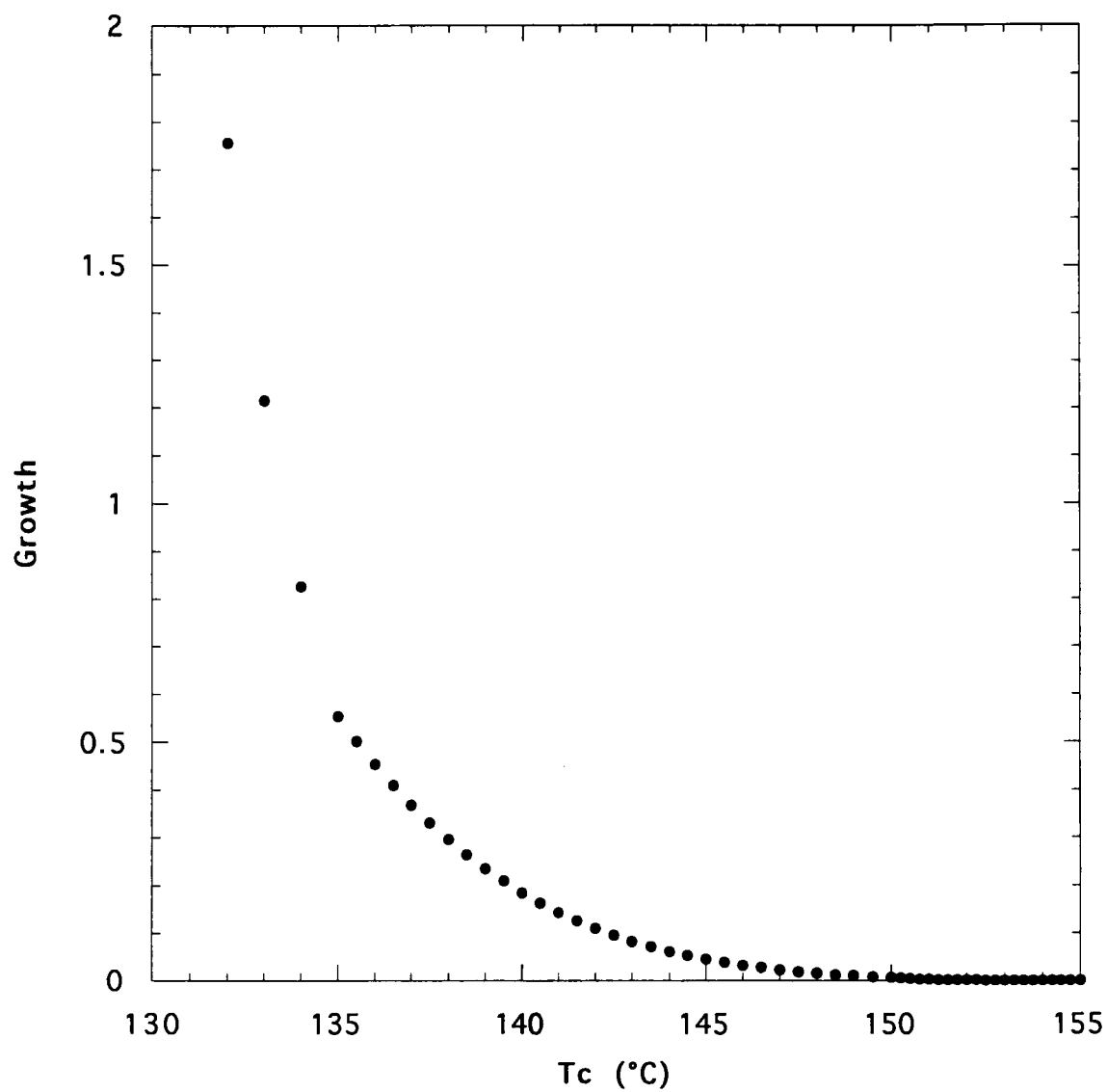


Fig.2.22 Growth rate versus temperature for an ideal polymer which has three regimes.

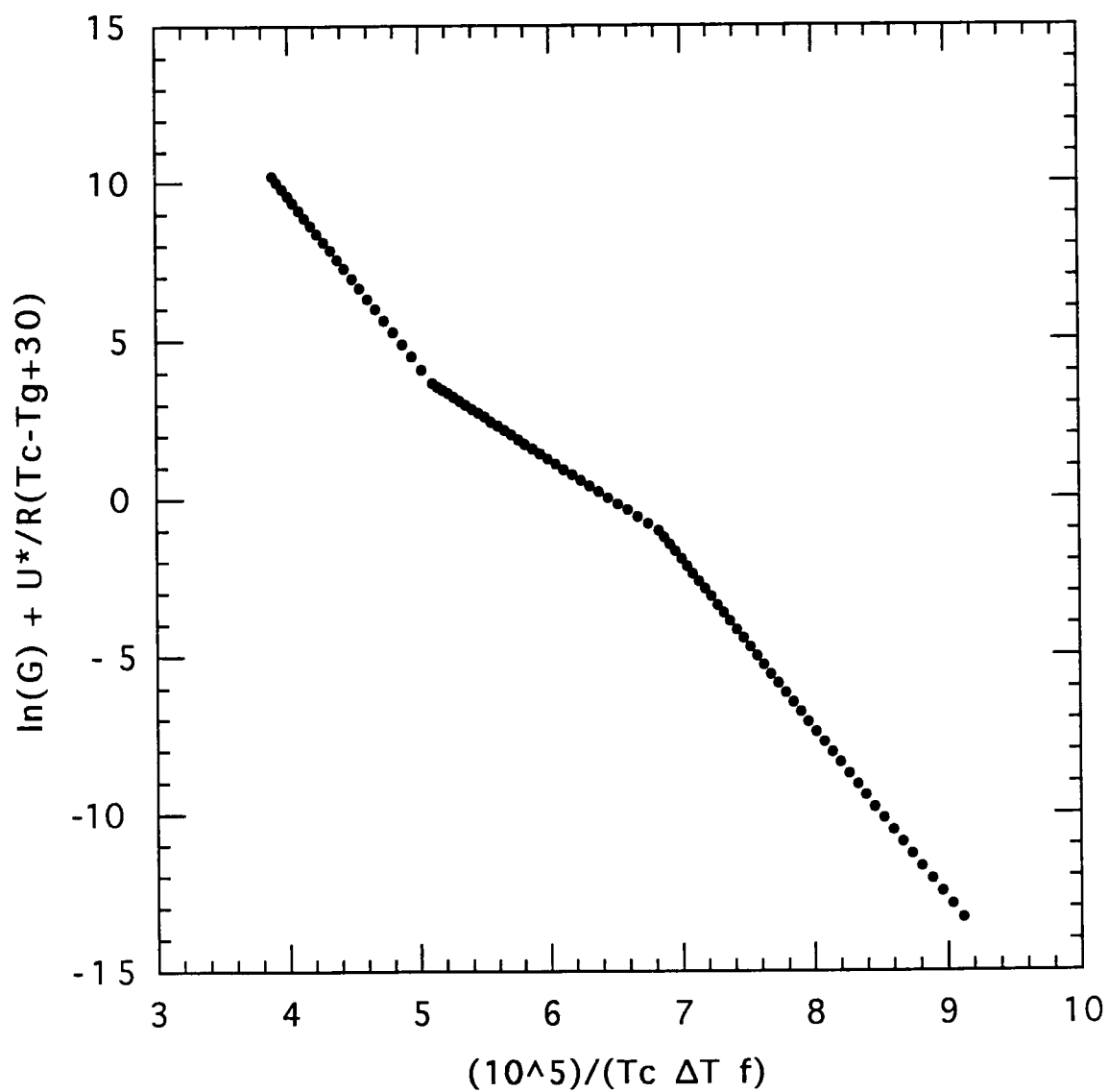


Fig.2.23 Analysis of the previous spherulitic growth (Fig.2.22) using the Lauritzen-Hoffman equation.

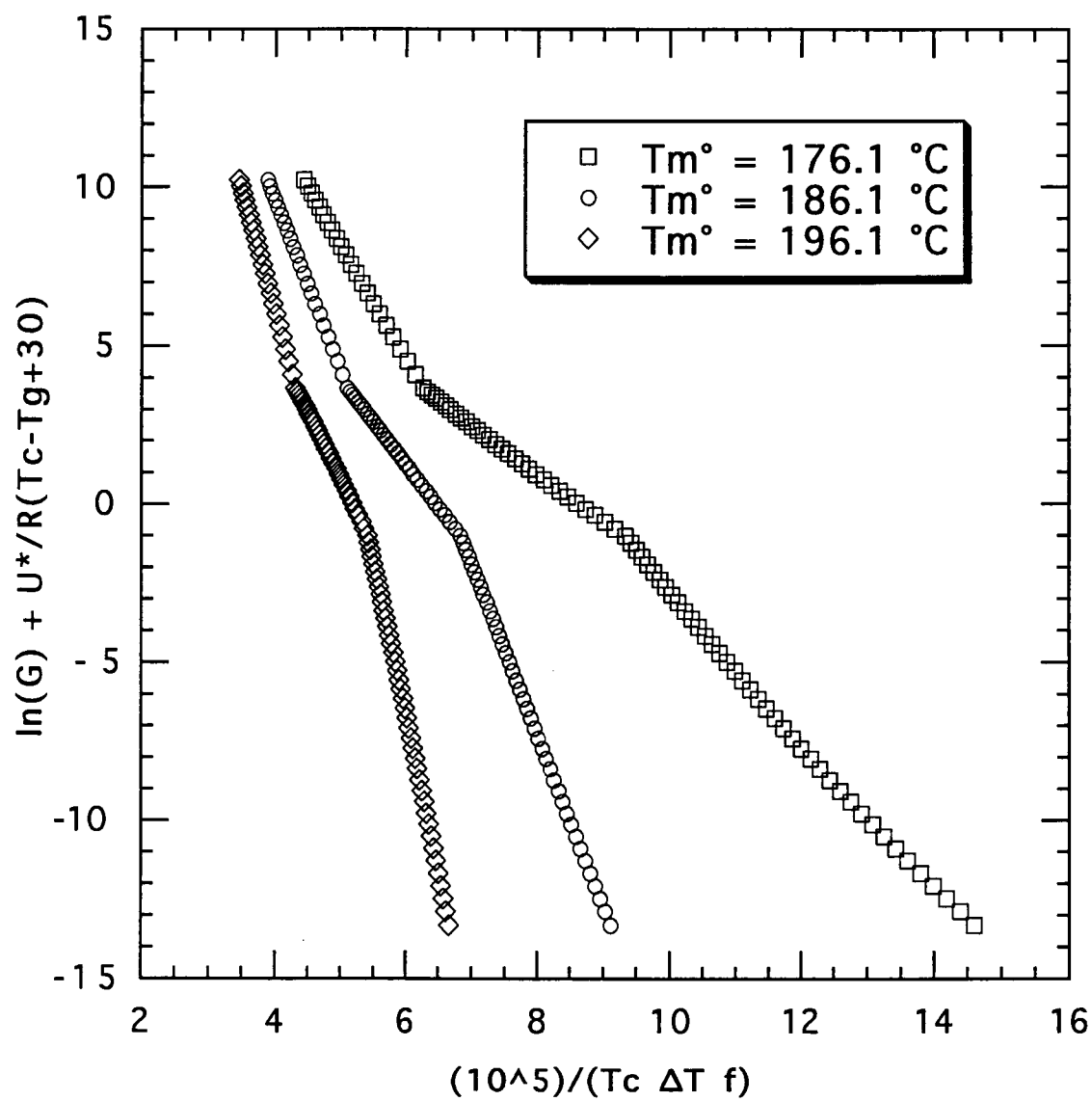


Fig.2.24 The effect of T_m° on Lauritzen-Hoffman analysis.

Table 2.5: Effect of T_m° on Lauritzen-Hoffman Analysis.

T_m° (°C)	Regime	Regime transition (°C)	K_g (K ²) 10^5	$\frac{K_{gIII}}{K_{gII}}$	$\bar{\sigma} \times \bar{\sigma}_e$ $\frac{\text{erg}^2}{\text{cm}^4}$	$\bar{\sigma}$ $\frac{\text{erg}}{\text{cm}^2}$	$\bar{\sigma}_e$ $\frac{\text{erg}}{\text{cm}^2}$	%error
176.1	I		2.351		446	10.0	44.6	55.4
176.1	II	135	1.524	1.5	578	10.0	57.8	42.2
176.1	III	150	3.608	2.4	684	10.0	68.5	31.5
186.1	I		5.388		1000	10.0	100.0	0.0
186.1	II	135	2.694	2.0	1000	10.0	100.0	0.0
186.1	III	150	5.388	2.0	1000	10.0	100.0	0.0
196.1	I		9.779		1776	10.0	177.6	77.6
196.1	II	135	4.246	2.3	1542	10.0	154.3	54.3
196.1	III	150	7.624	1.8	1384	10.0	138.5	38.5

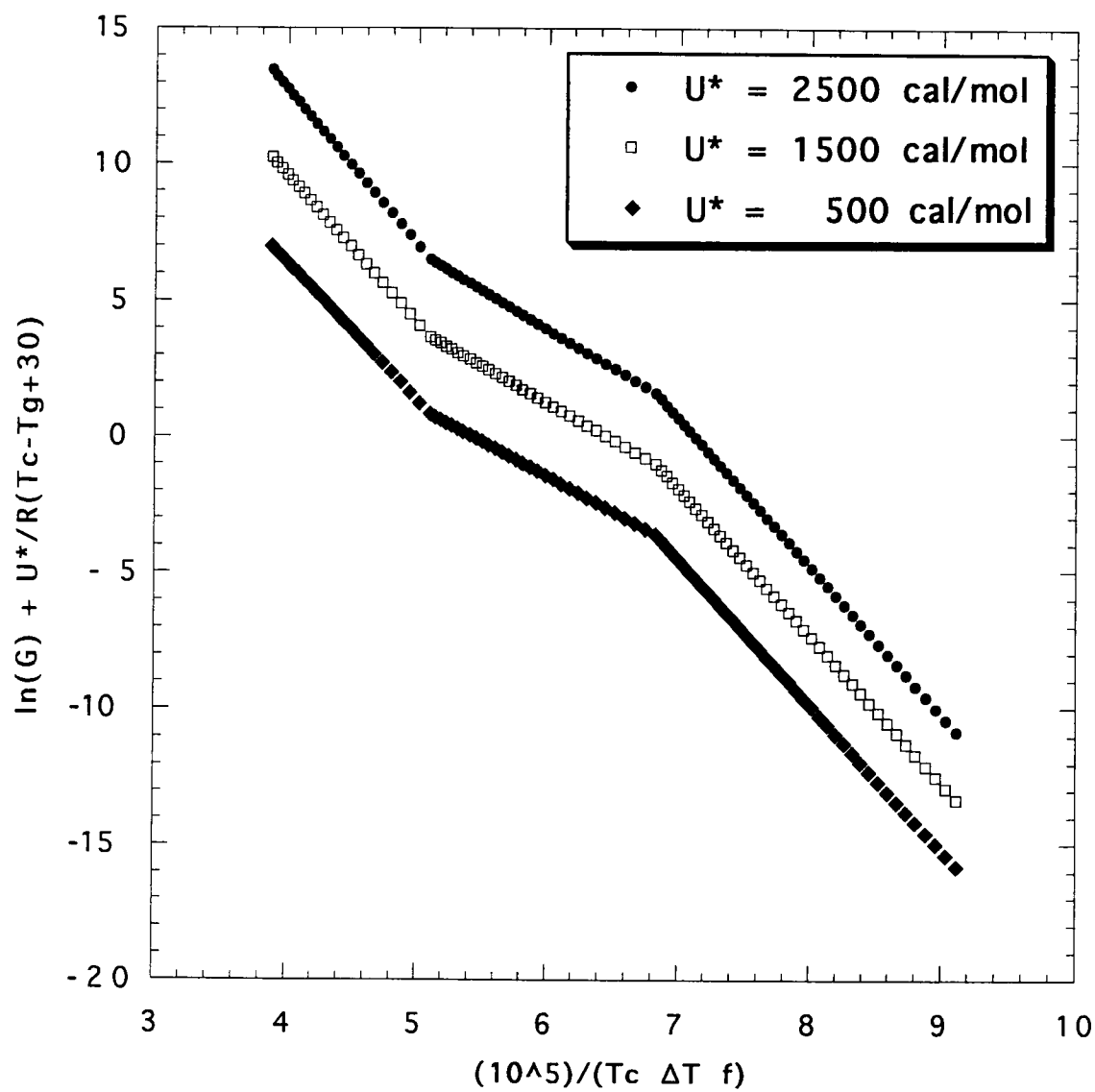


Fig.2.25 The effect of U^* on Lauritzen-Hoffman analysis.

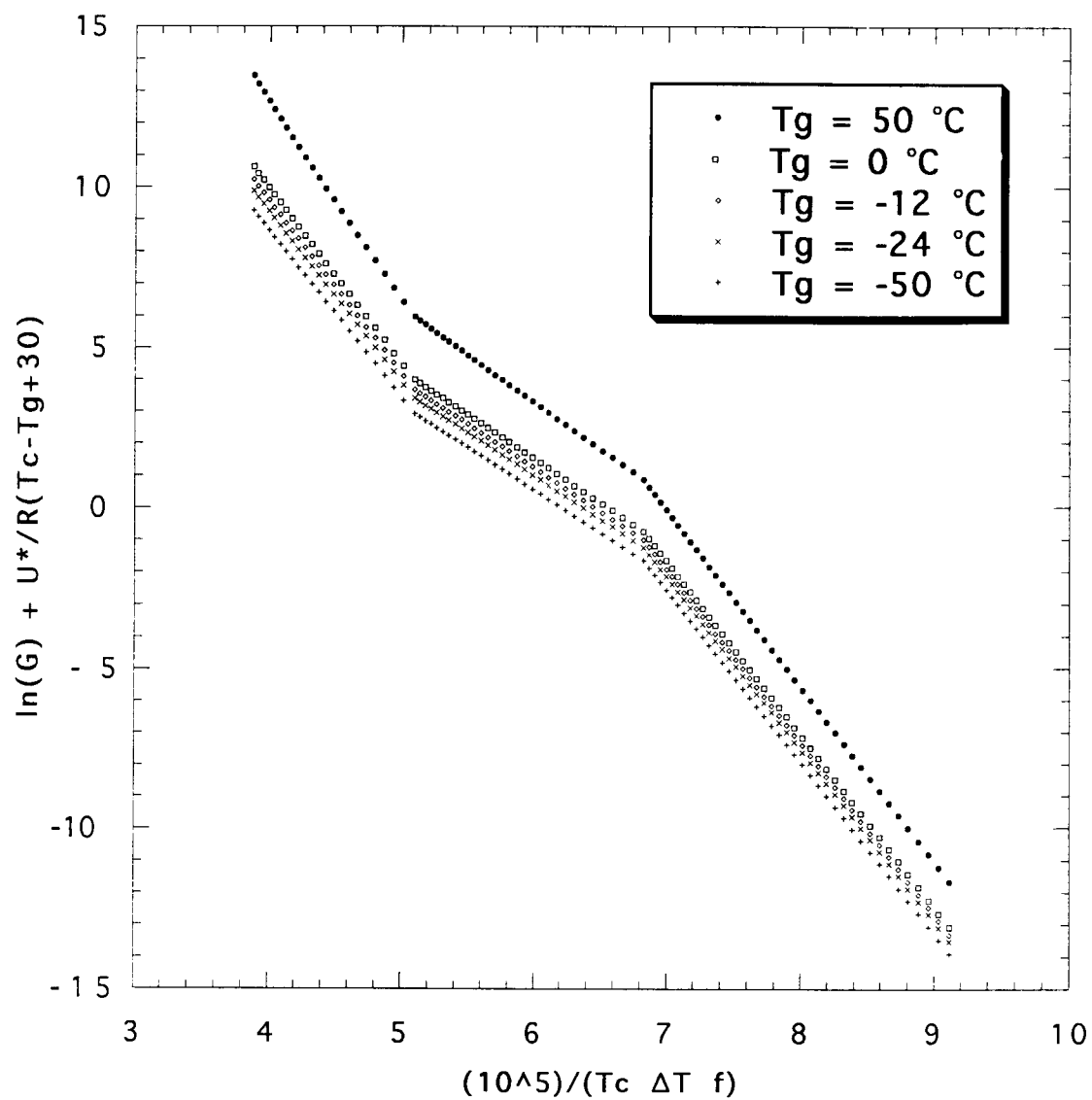


Fig.2.26 The effect of T_g on Lauritzen-Hoffman analysis.

2.3.2 Avrami Analysis

The Avrami equation was derived from prior work by Poisson based on expanding waves created by raindrops on a pond and results in the general equation:

$$1-v_c(t) = \exp(-Kt^n) \quad (2.7)$$

where, n is known as the Avrami index, and $v_c(t)$ is the crystalline volume fraction of the polymer. In general, n and K characterize the nucleation type and the crystal growth geometry. Theoretically, the Avrami index, n , can be derived as an integer which varies between 1 and 6 (Table 2.6), but due to the crystallization complexity, n is usually a decimal number. For better interpretation of the Avrami-index, one needs good information about nucleation, morphology and the mechanism of polymer crystallization.

There are several methods available for the study of bulk crystallization, including dilatometry, differential scanning calorimetry and x-ray diffraction. Optical microscopy is the most versatile method for the study of crystallization since the use of a trinocular permits the simultaneous measurement of bulk crystallization (using transmitted light intensity) and of crystal growth kinetics using direct observation.

Table 2.6: Theoretical values of n and K for different morphologies and nucleation mechanisms

Crystal Growth Shape	Nucleation Mode	Avrami Exponent (n)	Avrami Constant (K)
Rod	Heterogeneous	1	NGA
	Homogeneous	2	$\dot{N}GA/2$
Disc	Heterogeneous	2	$\pi NG^2 D$
	Homogeneous	3	$(\pi/3)\dot{N}G^2 D$
Sphere	Heterogeneous	3	$(4\pi/3)NG^3$
	Homogeneous	4	$(\pi/3)\dot{N}G^3$
Sheaf	Heterogeneous	5	-
	Homogeneous	6	-

- * A is constant area of the rod, D is thickness of the disc, G is linear growth rate, N is nucleation density and $\dot{N}$ is nucleation rate.
- * Heterogeneous means that number of spherulites is constant.
- * Homogeneous, also named sporadic, means that rate of nucleation of spherulites is constant.

Depolarized light microscopy, DLM, can be used to measure light intensity (I) as a function of time (t) and permits Avrami type analyses (Fig.2.27). From this type of experiment the volume fraction, $v_c(t)$, is not directly available; therefore, a relationship between the light intensity, I , and $v_c(t)$ is needed. If it is assumed that complete crystallization is reached at the maximum level of the plot (I versus t) then $v_c(t)$ is related to I as follows:

$$v_c(t) = I(t) = \frac{I - I_{\min}}{I_{\max} - I_{\min}} \quad (2.8)$$

Where $I(t)$ is the relative intensity at time t , and $I_{\min}$ and $I_{\max}$ are the minimum and maximum intensities, respectively. Equation 2.7 can be written in a logarithmic form as:

$$\ln[-\ln(1-I(t))] = \ln(K) + n \ln(t) \quad (2.9)$$

The values of n and K can be determined from the plot of $\ln[-\ln(1-I(t))]$ versus $\ln(t)$; n is the slope, and $\ln(K)$ is the intercept.

In reality, polymer crystallization is too complex to be described by a simple expression such as the Avrami equation. For example, the assumption in Avrami's expression that the volume does not change is inaccurate because the specimen tends to shrink during crystallization. In addition, secondary crystallization and crystal perfecting processes are not taken into account.

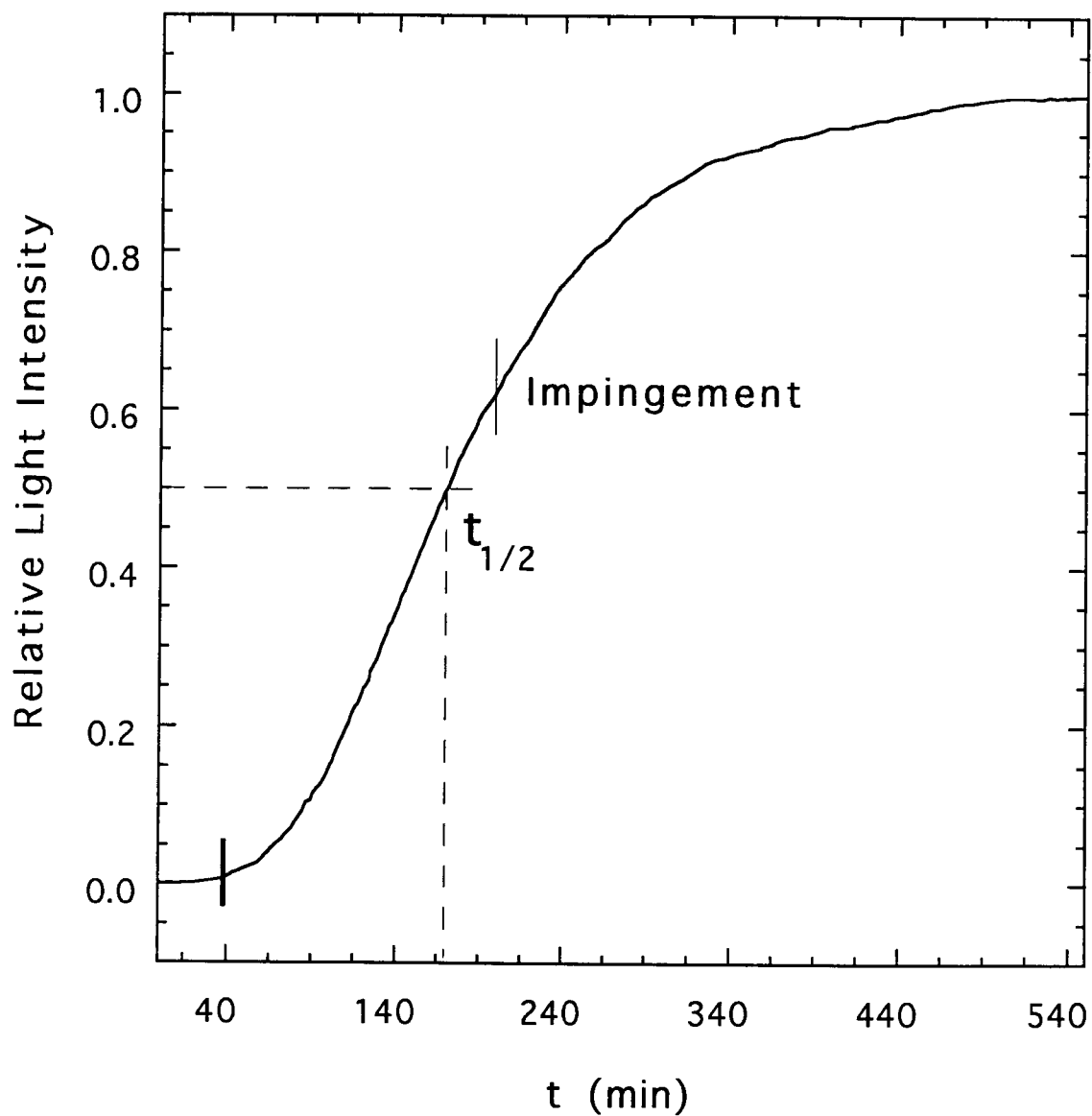


Fig.2.27 Typical light intensity (I) as a function of time (t) during crystallization of a polymer using depolarized light microscope, DLM.

2.4 Scattering

The rheoptical behavior of polymers can be investigated by many different methods, therefore, it is important to recognize what information is being measured versus what information is sought before applying any of these. Rheoptical methods provide information on a level that is often correlated with the wavelength that is involved with a particular method (Fig.2.28). For example, x-ray scattering, which utilizes wavelengths in the range of 0.1-0.3 nm, provides information on a scale of 0.1 to tens of nanometers, depending on whether WAXS or SAXS is utilized. However, the angular range over which the information is gathered is also of extreme importance for rheoptical methods.

Wide angle x-ray diffraction, WAXD, and small angle x-ray scattering, SAXS, are two powerful techniques that reveal information about the internal structures of materials, in particular of polymers. In the literature, WAXD is found to be mostly useful for determining the lattice parameter from the d-spacing of the reflecting planes. Sometimes, a prior knowledge of the material's structure can be used along with the WAXD to determine crystal's dimension and orientation. The SAXS is mostly used to disclose information about a larger scale. Depending on the geometrical set up of the experiment, SAXS can be used to estimate the lamellar thickness, crystal size, and radius of gyration.

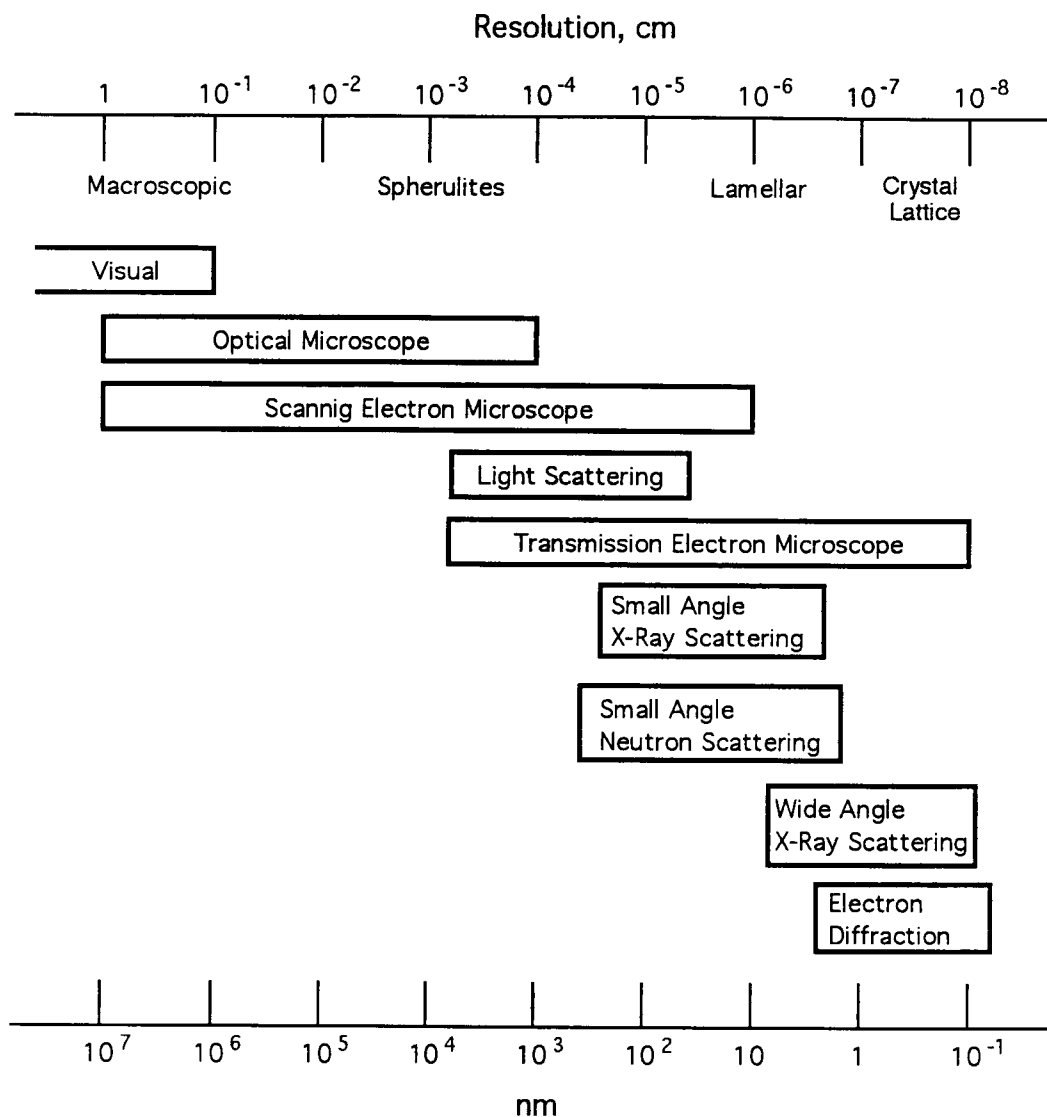


Fig.2.28 Resolving power of structural characterization technique, including scales with respect to the types of structure found in polymeric materials.

Since the scattering is done in reciprocal space, a correlation function is needed to connect the reciprocal space to the real space.

The basics of scattering for either SAXS or WAXS is due to the scattering of single atoms. A single atom scatters an incident beam of x-rays in all directions in space. A large number of atoms arranged in a perfectly periodic array in three dimensions, to form a crystal, scatters (diffracts) x-ray in relatively few directions. It does so precisely because the periodic arrangement of atoms causes destructive interference of the scattered rays in all directions except those predicted by the Bragg's law, and in these directions constructive interference (reinforcement) occurs.

2.4.1 Wide Angle X-Ray Diffraction

Wide angle x-ray diffraction, WAXD, is mostly used to determine the crystalline structure of a material using Bragg equation:

$$n\lambda = 2d_{hkl} \sin\theta \quad (2.10)$$

Where n is an integer indicating the order of scattering and d_{hkl} represents a specific crystallographic interplanar spacing as defined by the indexes h , k , and ℓ . θ is the Bragg angle.

Like density and thermal analysis, wide angle x-ray diffraction measurements have been used to determine the degree of crystallinity in polymeric systems. However, the x-ray technique is the only one to examine crystallinity (three-dimensional order) directly; all other techniques measure properties related to the degree of crystallinity. But there are still problems with absolute crystallinity measurements even for the most rigorous methods, owing to the arbitrary nature of constructing the baseline delineating crystalline and amorphous scattering.

The method involves determining the area under all peaks in relation to a baseline. An arbitrary "amorphous peak" is drawn underneath the prominent crystalline peaks. The crystallinity (X_c) is determined with the following equation:

$$X_c = \frac{A_c}{A_{total}} = \frac{(A_{total} - A_a)}{A_{total}} = 1 - \frac{A_a}{A_{total}} \quad (2.11)$$

where A_{total} is the area between the peaks and the baseline; A_a is the amorphous area.

Known errors are a matter of determining how the baseline of the diffractometer output is defined relative to the actual crystalline peak area and the area attributed to amorphous peaks (Fig.2.29).

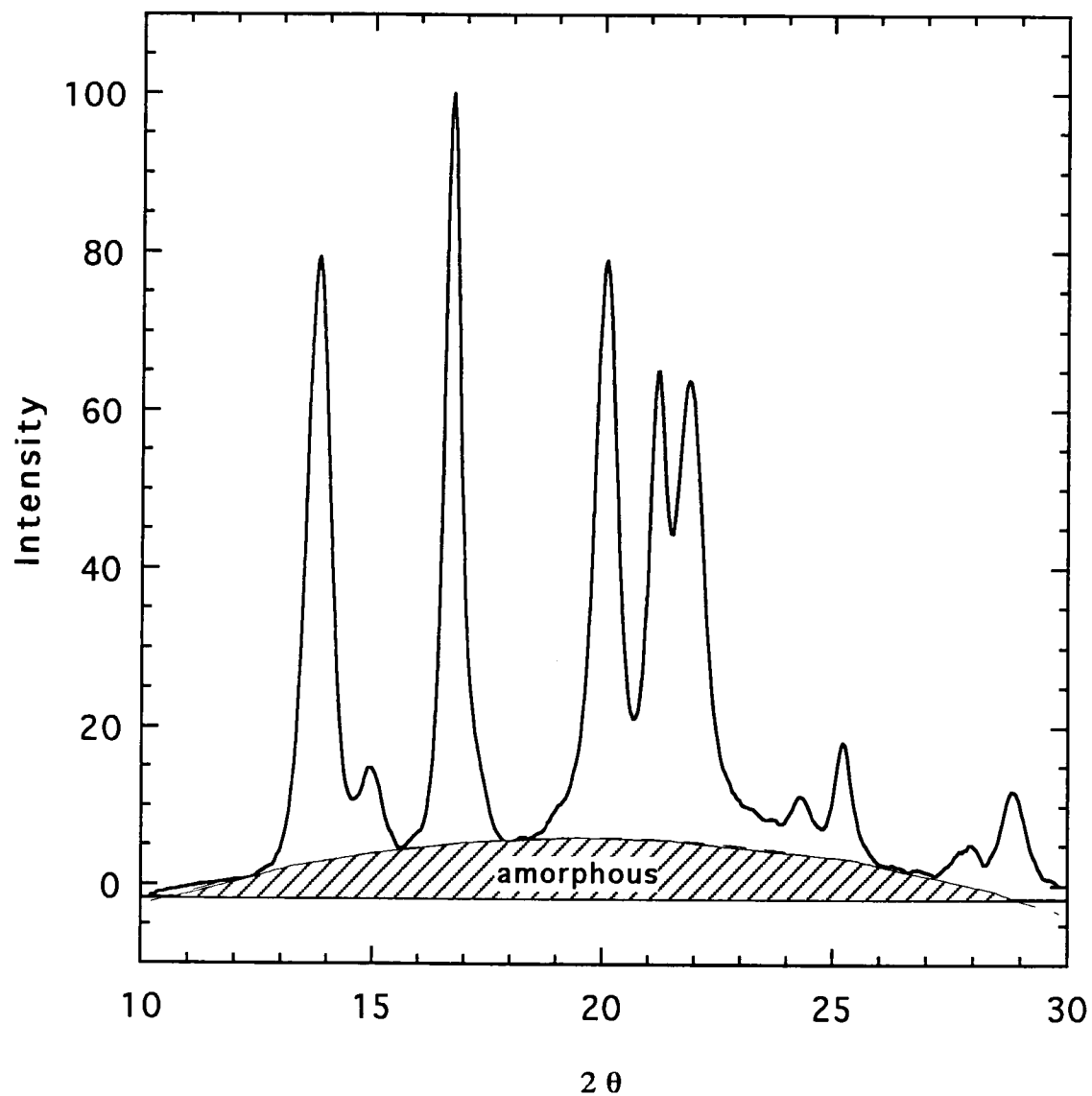
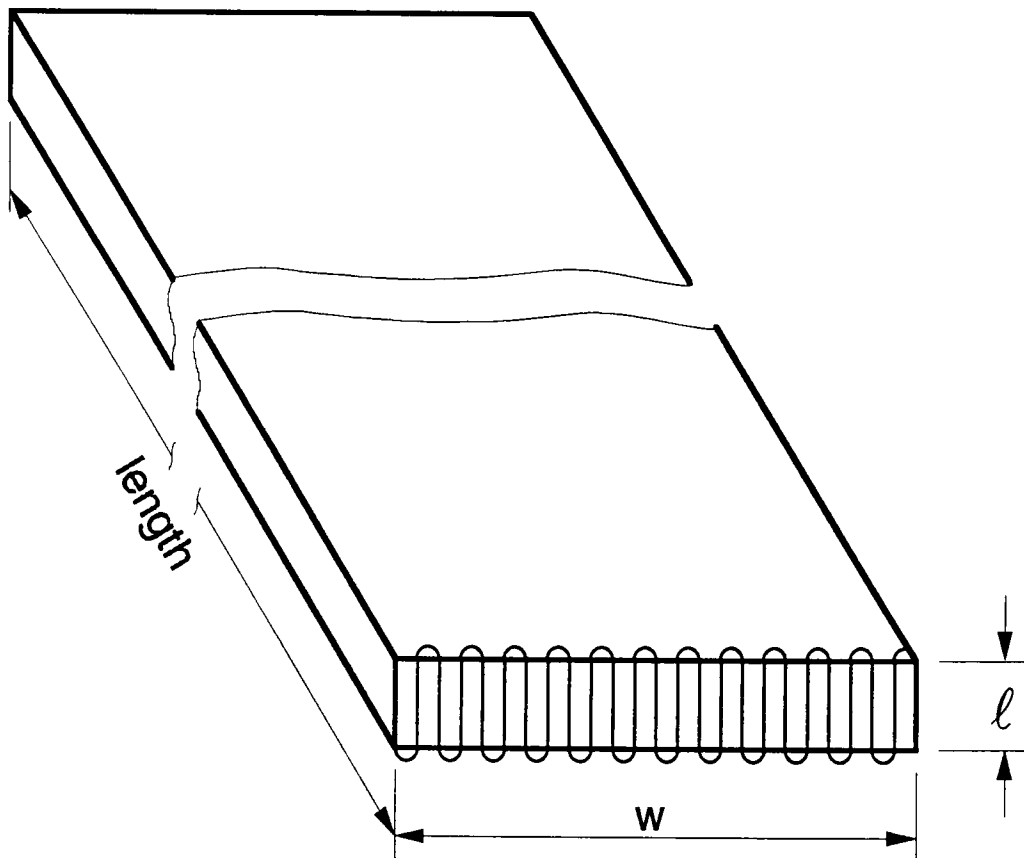


Fig.2.29 Wide angle x-ray diffraction of iPP (γ -form). The amorphous contribution is represented by the shaded area.

2.4.2 Small Angle X-Ray Scattering

It is well established that, when crystallized from the melt, polypropylene forms lamellar structure regardless of whether it is crystallized under quiescent or stress-induced conditions [12]. Lamellae are defined as ordered structures that contain polymer molecules in the form of platelets or ribbons usually in the range of 20 to 500Å thick (Fig.2.30). Since polypropylene is a semicrystalline polymer, some of the amorphous region is trapped between adjacent lamellae forming stacks of ordered and disordered regions (Fig.2.31).

Stacked lamellar textures can be viewed as periodic fluctuations in electron density caused by the differences in the densities of the amorphous and crystalline phases. Structural characterization of these systems can be obtained by SAXS [120-123]. This density fluctuation generates x-ray scattering at very small angles, typically less than 1° with Cu K α wavelength. An important parameter often obtained is the so-called long spacing (L), which relates to the center-to-center distance of the stacked lamellae averaged over the material (Fig.2.31). This long spacing promotes a scattering maximum or peak when measured in an unoriented lamellar morphology (Fig.2.32).



ideally $l \ll w \ll \text{length}$

Fig.2.30 Schematic drawing of lamellar structure.

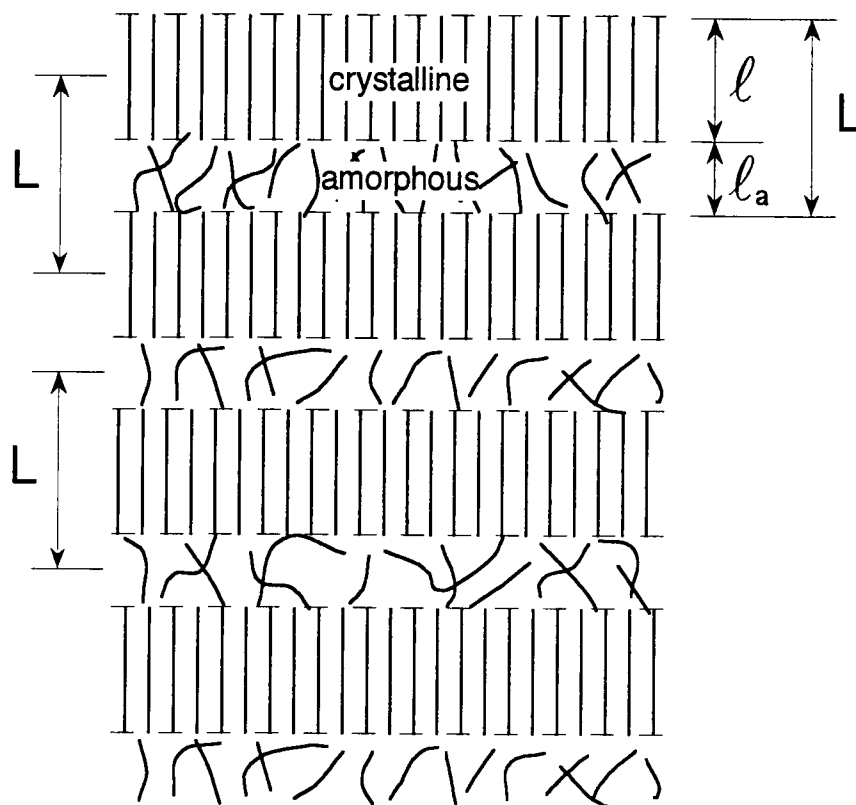


Fig.2.31: Model of semicrystalline materials.

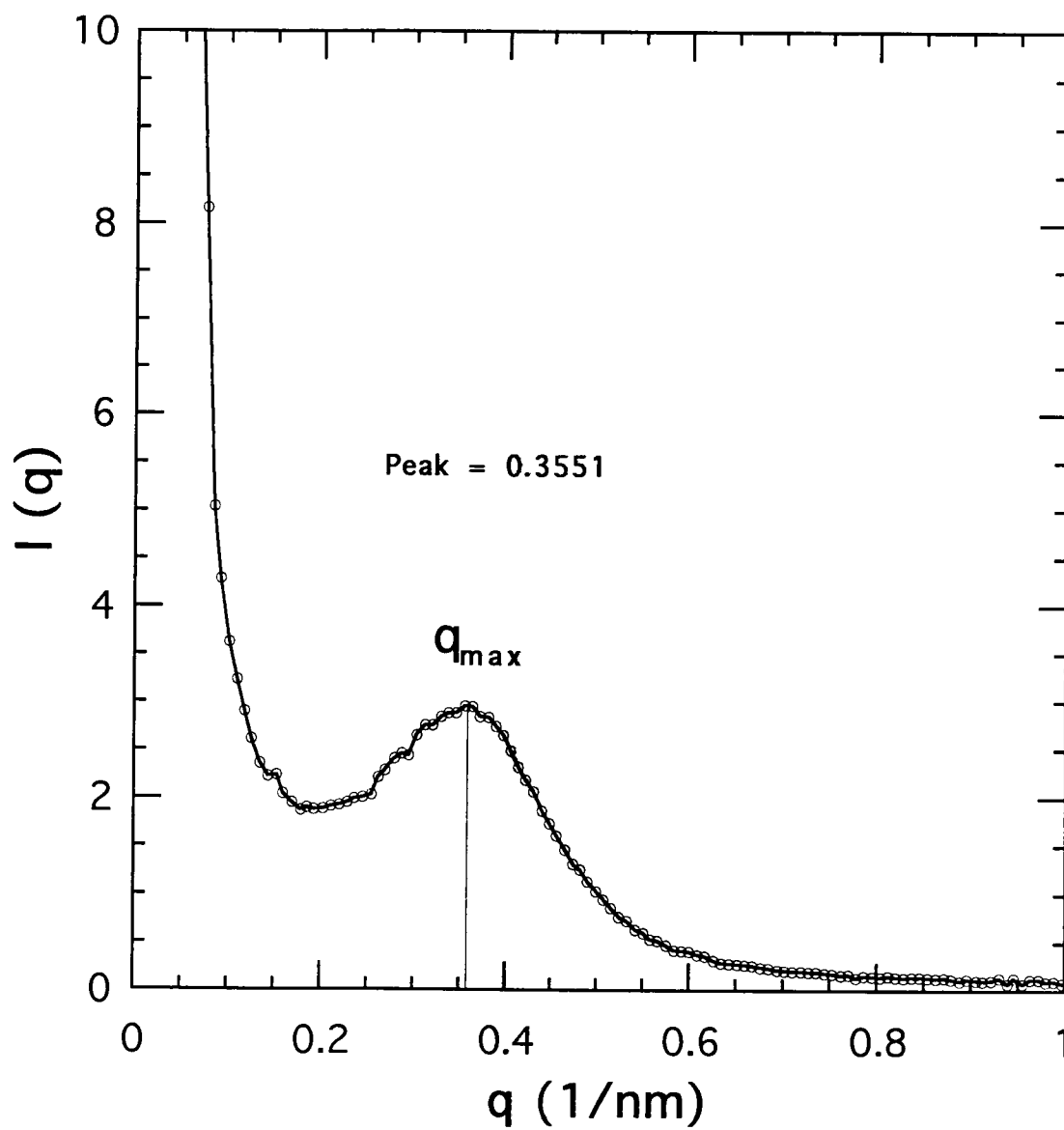


Fig.2.32 Small angle x-ray scattering of semicrystalline materials (iPP).

A given long spacing, as often estimated by applying the Bragg equation to the intensity maximum at a specific angle (equ.2.12), is not a direct measure of the lamellar thickness but only an estimate of the interlamellar spacing. Without a knowledge of the thickness of the amorphous layer separating the lamellae, the long spacing value is only an index of the periodicity caused by the lamellar texture.

$$L = \frac{2\pi}{Q_{\max}} \quad (2.12)$$

The measurement and interpretation of SAXS data are more often complicated than those of WAXS data from semicrystalline materials. This follows from the Babinet principle of reciprocity, which states that it is impossible to distinguish by angular scattering between a system of particles in space and a corresponding system in which the particles and the space have been exchanged. However, with some additional knowledge of the system by other techniques, SAXS can often provide much insight into structural details.

Figure 2.33 shows the scattering vectors of two particles at a distance r from each other. If the scattering is coherent, which means that the amplitudes are added, then the intensity is given by the absolute square of the resulting amplitude (F). The amplitudes are of equal magnitude, and differ only by their phase ϕ , which depends on the position of the electron in space.

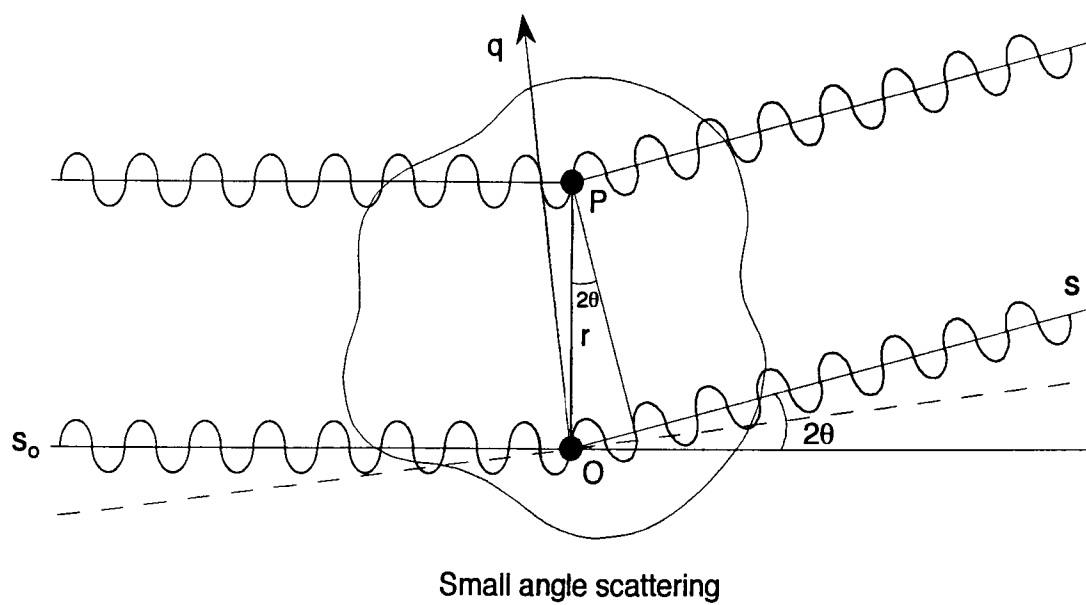


Fig.2.33 Scattering vectors of two particles at a distance r from each other.

$$\varphi = \frac{2\pi}{\lambda} r (s - s_0) \quad (2.13)$$

where s is the scattered beam, s_0 is the incident beam, λ is the wave length, and r is the path difference of a point P against the origin O (Fig.2.33). φ takes the form: $\varphi = -\mathbf{q}\mathbf{r}$ where:

$$q = \frac{4\pi}{\lambda} \sin\theta \quad (2.14)$$

Here θ means half the scattering angle.

The vector product $\mathbf{q}\mathbf{r}$ means that only the component of $\mathbf{r}$ in $\mathbf{q}$ is relevant for the phase. So all points in a plane perpendicular to $\mathbf{q}$ will have the same phase.

The resulting amplitude, F , of the scattering particles can be obtain by summing up all secondary waves, represented by a term $e^{-i\mathbf{q}\mathbf{r}}$ each. The amplitude of diffraction in a certain direction (specified by $\mathbf{q}$) is the Fourier transform of the electron density distribution $\rho(\mathbf{r})$ within the object.

$$F(\mathbf{q}) = \iiint \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} dV \quad (2.15)$$

The electron density $\rho(\mathbf{r})$ is defined as the number of electrons per unit volume.

The intensity $I(\mathbf{q})$ is the absolute square of $\mathbf{F}$.

$$I(\mathbf{q}) = \mathbf{F} \mathbf{F}^* = \iiint \iiint \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} dV_1 dV_2 \quad (2.16)$$

Equation (2.16) is a double integration over V_1 and V_2 . Consequently, this complex mathematical equation can be achieved by two different steps: first to summarize all pairs with equal relative distance, and then to integrate over all relative distances, including the phase factor.

The first step is the auto-correlation, defined by:

$$\tilde{\rho}^2(\mathbf{r}) \equiv \iiint \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) dV_1 \quad (2.17)$$

where $\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2) = \text{constant}$

The second step consists of an integration over the C-space:

$$I(\mathbf{q}) \equiv \iiint \tilde{\rho}^2(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} dV \quad (2.18)$$

So the intensity distribution in $\mathbf{q}$ or reciprocal space is uniquely determined by the structure of the object.

The result will be the same, when $\mathbf{r}$ is enlarged and $\mathbf{q}$ is diminished by the same factor. So large particles will give a diffraction pattern concentrated at small angles.

In order to simplify the problem of small angle scattering, two restrictions are introduced:

(1) The system is statistically isotropic.

(2) There exists no long range order. This means that there is no correlation between two points separated widely enough.

From restriction (1), the phase factor $e^{-i\mathbf{q}\cdot\mathbf{r}}$ can be replaced by its average, taken over all directions of $\mathbf{r}$, as expressed by the fundamental formula of Debye (1915):

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}} \rangle = \frac{\sin qr}{qr} \quad (2.19)$$

Equation 2.18 is, therefore, reduced to the form

$$I(q) \equiv \int 4\pi r^2 \tilde{\rho}^2(r) \frac{\sin qr}{qr} dr \quad (2.20)$$

It is convenient to use the electron density fluctuation $\eta = \rho - \bar{\rho}$ instead of the density ρ itself. The auto-correlation (2.17) is then defined as:

$$\tilde{\eta}^2 = (\rho - \bar{\rho})^2 = \tilde{\rho}^2 - V\bar{\rho}^2 = V\gamma(r) \quad (2.21)$$

Where $\gamma(r)$ is the correlation function

$$\gamma(r) = \langle \eta(r_1) \eta(r_2) \rangle \quad (2.22)$$

with $r = |\mathbf{r}_1 - \mathbf{r}_2| = \text{constant}$, also with the property $\gamma(0) = \overline{\eta^2}$, and $\gamma \rightarrow 0$ for large r .

The most general formula for the diffraction of systems obeying restrictions (1) and (2) is:

$$I(q) = V \int_0^{\infty} 4\pi r^2 \gamma(r) \frac{\sin qr}{qr} dr \quad (2.23)$$

$\gamma(r)$ is found by the inverse Fourier transform:

$$V\gamma(r) = \frac{1}{2\pi^2} \int_0^{\infty} q^2 I(q) \frac{\sin qr}{qr} dq \quad (2.24)$$

$$I(0) = V \int_0^{\infty} 4\pi r^2 \gamma(r) dr \quad (2.25)$$

$$V\gamma(0) = \frac{1}{2\pi^2} \int_0^{\infty} q^2 I(q) dq = V\overline{\eta^2} \quad (2.26)$$

If, for example, parts of the system were shifted or deformed, the diffraction pattern might be altered considerably, but the integral in Equ.2.26 must remain invariant.

Invariant:
$$Q = \int_0^{\infty} q^2 I(q) dq \quad (2.27)$$

Also, among the directly obtainable parameters is the distance distribution function, $p(r)$, defined as:

$$p(r) = r^2 \gamma(r) = \frac{1}{2\pi^2} \int_0^{\infty} qr I(q) \sin(qr) dq \quad (2.28)$$

The data collected from the SAXS experiment is limited to a small range of q , and the correlation function $\gamma(r)$ requires data from zero to infinity. There are two approaches to the problem. One is to extrapolate $I(q)$ to low values of q and high values of q using different approximations so that the whole range of q is covered. The second technique is to assume a model for scattering and determine the scattering intensity [124-128]. When allowing the parameters of the model to vary, the shape of the intensity curve changes accordingly. If the model is very close to the reality then the intensity curve will be similar to the experimental one. To determine the fidelity of the model, it has to be tested for different samples, which are prepared differently.

Theoretical SAXS has been well established for dilute systems where the scattering particles have spherical shape. For example, using Guinier approximation for low values of q , the radius of gyration of the particle can be determined. But, since the system of concern is dense and has long range order then none of the classical held views of the small angle scattering can describe this system. Nevertheless, in practice, Guinier and Porod approximations have been used extensively because of their simplicity (Fig.2.34).

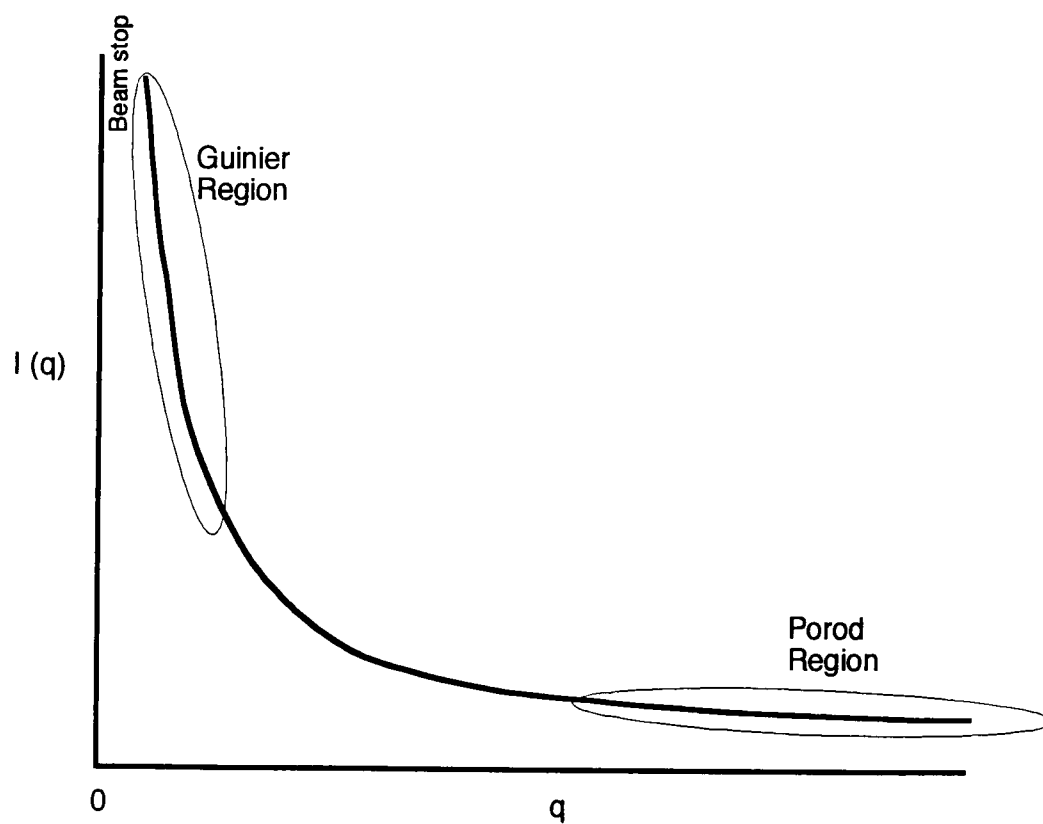


Fig.2.34 Guinier and Porod regions in the SAXS.

Guinier Approximation

For low values of q Guinier approximated the scattering intensity of spherical particle from dilute solution as follows:

$$I(q) = (\Delta n_e)^2 e^{-q^2 R^2/3} \quad (2.29)$$

where R is the radius of gyration. $R = \sqrt{r^2}$

A plot of $\ln(I(h))$ versus h^2 would generate a slope of $(-R^2/3)$.

Porod Approximation

Porod, on the other hand, approximated the scattering intensity of particles (with any shape) for high values of q as follows:

$$I(q) = \frac{(\rho - \rho_o)^2}{8\pi^3} \frac{S}{q^4} \quad (2.30)$$

Where S is the surface area of the scattering particle.

When intensities of high values of q are available, Porod approximation can be tested by plotting $\ln(I)$ versus $\ln(q)$. The slope of the line must be (-4) ; otherwise, Porod's equation is not valid, and the scattering is due to Fractal phenomenon.

2.4.3 Small Angle Neutron Scattering

This technique is based on elastic scattering by isotropically distinct guest molecules introduced into a host matrix. Usually hydrogen is replaced by deuterium. Because they possess zero charge, neutrons interact weakly with matter and penetrate it easily. Depending on the angular range investigated, neutron scattering data can provide information on size, shape, and trajectory of a single polymer molecule [129-136]. SANS provides information on global chain conformation. At very low angles, the radius of gyration of the tagged molecules can be obtained. Finer details are seen at higher angles of scattering. Intermediate angle NS reveals the short-range order of tagged stems. Two problems are encountered in the use of NS for the investigation of polymer crystallization. One is the segregation of the tagged molecules upon crystallization. The other is that models have to be assumed to calculate their patterns, which are then compared with experimental data. Usually Monte Carlo simulation is used [137]. To avoid segregation, researchers often resort to quenching.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

Isotactic polypropylenes, iPP, were supplied by Exxon Corporation and had an isotacticity of >99% as determined by Exxon using NMR methods. The values of M_n , M_w and M_z were respectively 72K, 257K, and 528K. The material was supplied as small cylindrical pellets with an average size of 3mm in diameter and 3mm in height.

The deuterated polypropylene was supplied as powder by Dr. John Rabolt of IBM Corporation. The values of M_n , M_w and M_z were 98.6K, 258K, and 522K, respectively.

Sample Preparation

The polymer samples were first prepared as thin films using a Wabash model 12-12-2TB 12-ton melt press. The resin pellets or powder were placed between two clean sheets of Kapton which intern were placed between two stainless steel platens. The whole set was positioned between the preheated mobile and fixed plates of the press. The polymer chips were allowed to melt at a temperature of 200°C for about five minutes and then pressed with an applied pressure of about 0.8 ton/in² for two minutes. Later, the polymer sample was taken out and allowed to cool at room temperature. Usually, a

0.1 mm thick film is obtained by this process. If a thinner film is required then more time in the press under pressure is allowed.

3.2 Differential Scanning Calorimeter

A Perkin-Elmer series 7 Differential Scanning Calorimeter, DSC, was used to determine the equilibrium melting point of iPP. The DSC was calibrated using pure indium as a standard ($T_m = 156.60\text{ }^{\circ}\text{C}$). The calibration was checked every three to four hours to make sure that the accuracy was better than 0.02°C . The sample was heated to 200°C and held for ten minutes, in order to lose its thermal history, then it was rapidly cooled at a rate of $80\text{ }^{\circ}\text{C}/\text{min}$ to the desired crystallization temperature, T_c . The sample was held at the crystallization temperature for 10 to 70 minutes depending on T_c , so that enough time was given to grow small crystals, then melted at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. Two melting points, the peak and the modified return-to-the-baseline (MRB), were taken each run (Fig.3.1).

All samples were prepared under the flow of nitrogen gas during melting and crystallization to prevent the degradation of the polymers.

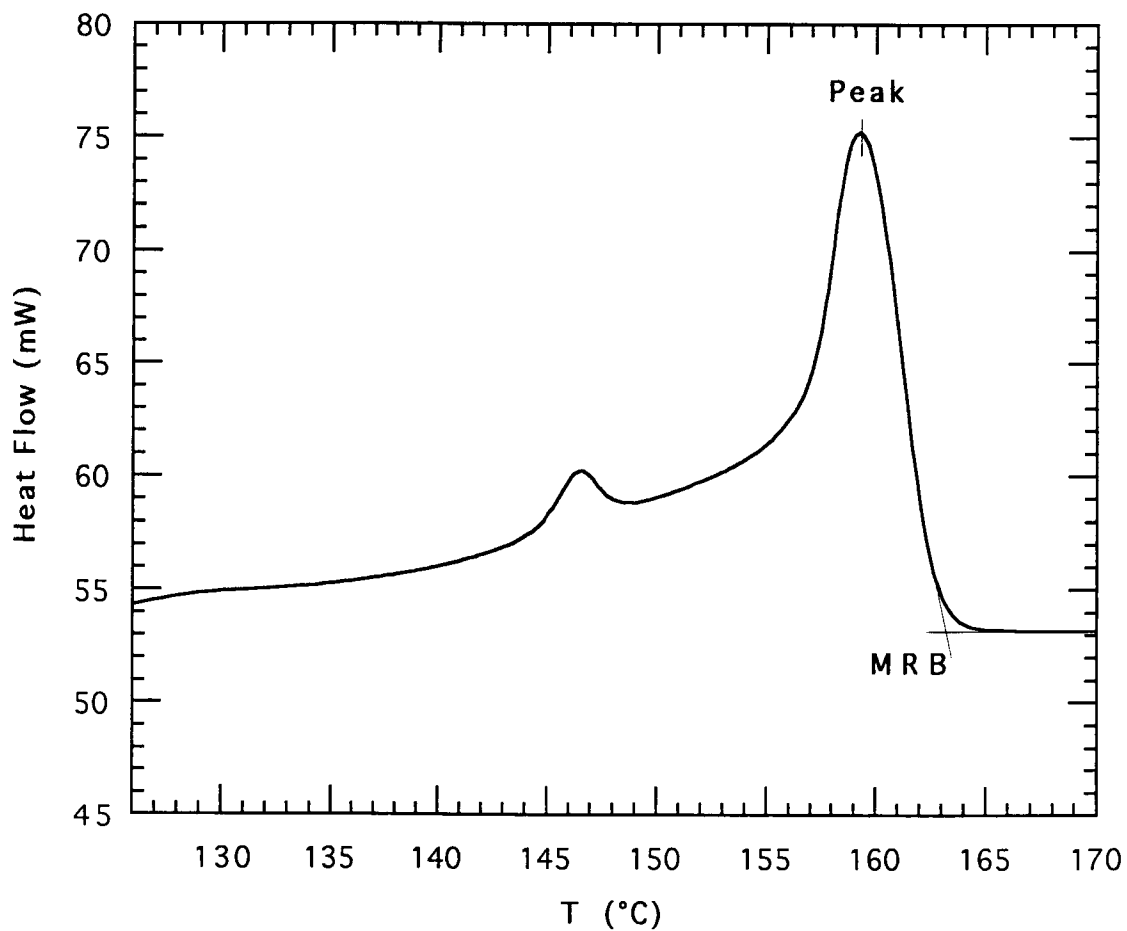


Fig.3.1 Typical melting curve from the DSC experiment. The peak and the modified return-to-the-baseline (MRB) are shown.

3.3 Depolarized Light Microscope

Transmitted light intensity determinations of melting point were carried out using a Mettler hot stage mounted on an Olympus microscope under cross-polar conditions. A trinocular was used; one beam passing to a photo-multiplier tube attached to a chart recorder and the second to a binocular eyepiece for direct observation (Fig.3.2). The hot stage was calibrated using an Omega, type J, calibrated thermocouple (Fig.3.3 and Fig.3.4). The polymer sample was placed between two glass cover slips. Using another hot stage the sample was heated to 200°C and held for ten minutes then rapidly transferred to the hot stage which was set to the desired crystallization temperature. This procedure assured the isothermal crystallization of the polymer. For each run the sample was crystallized and then heated at a rate of 10°C/min, and the melting point of the polymer was recorded.

Recording the melting temperature can be done with two different ways. The easiest way is using chart recorder which is connected to a photo-multiplier tube, the melting temperature is the point at which the light intensity is minimum. The minimum intensity point is hard to define; therefore, modified return to base line is used. The other method that can be used to determine the melting temperature is by using a stop-watch while looking to the fading spherulite through the microscope. Both methods reveal

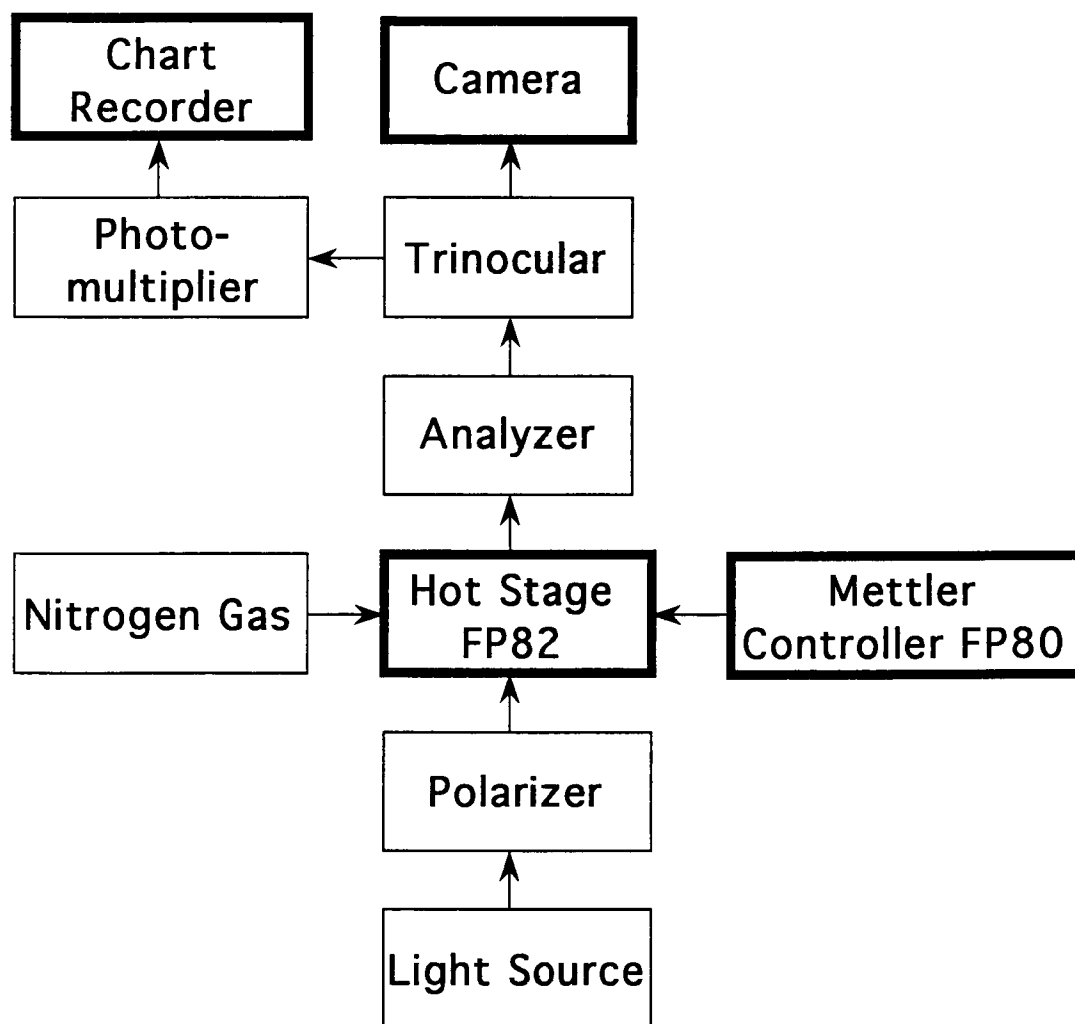


Fig.3.2 Simplified schematic of depolarized light microscopy, DLM.

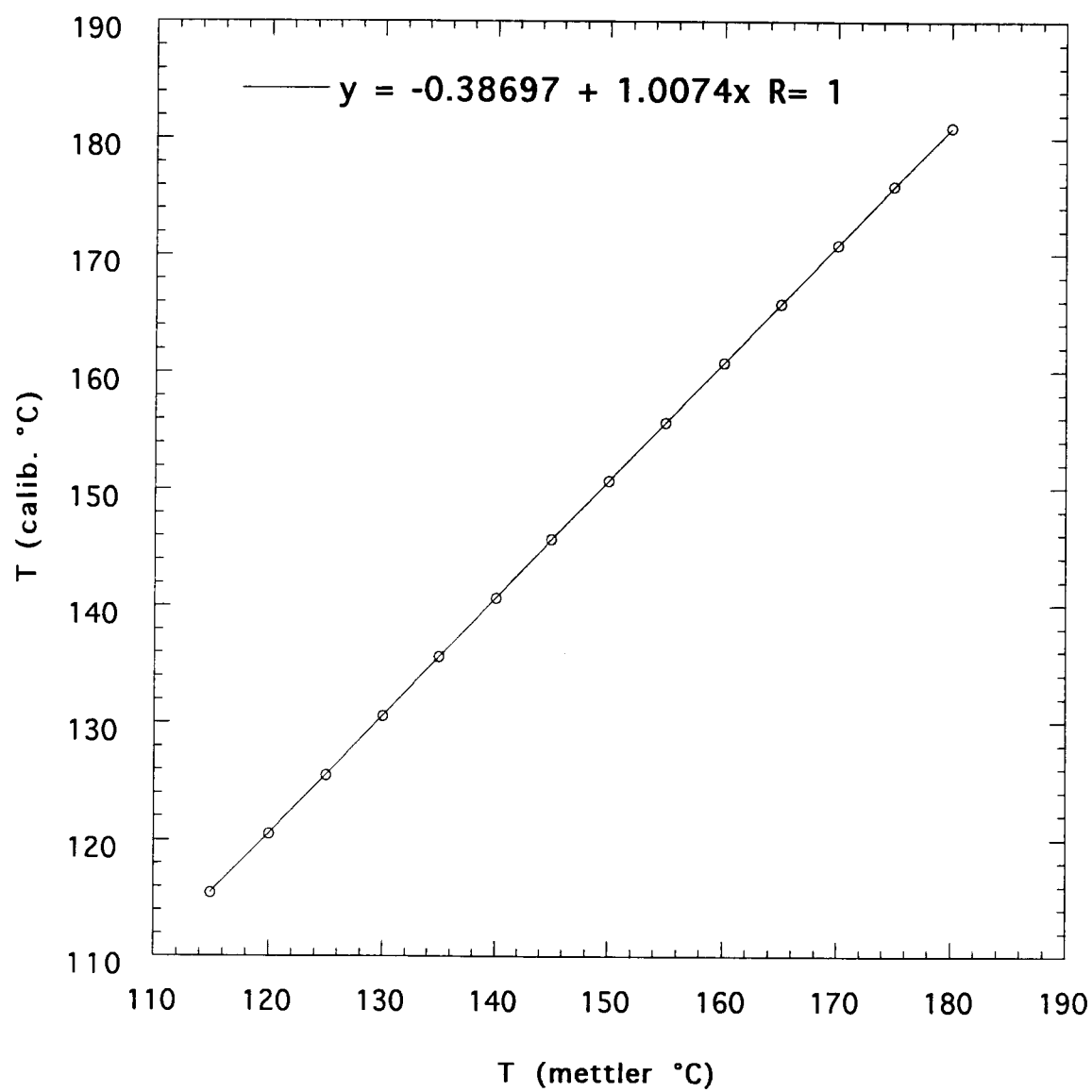


Fig.3.3 Temperature calibration of the hot stage.

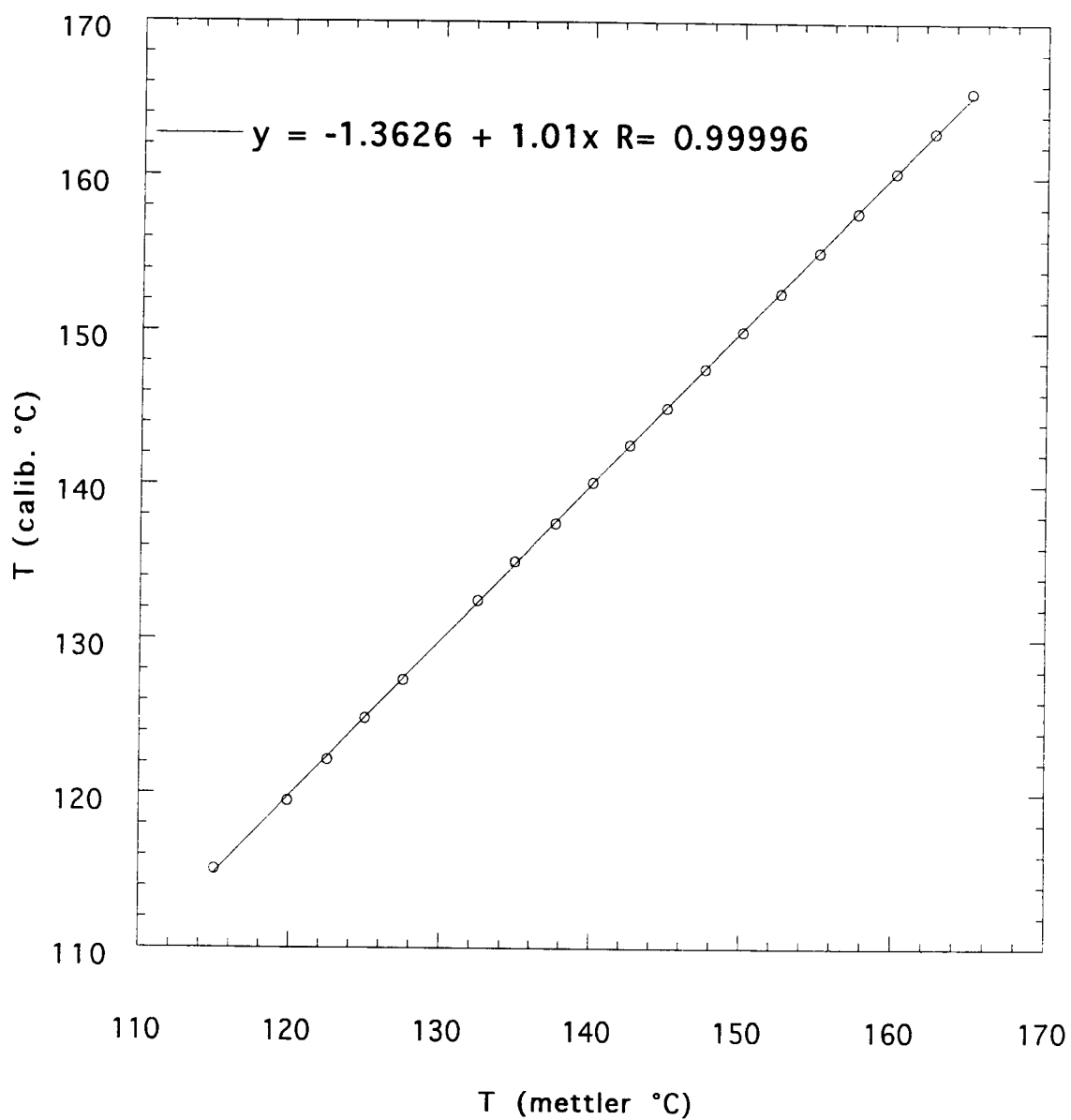


Fig.3.4 Rate calibration of the hot stage.

similar results, but the first one can not be used if the light intensity is low. As a result, the former method is not used for determining the melting temperature from small spherulites. Using the second method, the melting temperature is determined simply by using the following equation.

$$T_m = T_c + t \times R \quad (3.1)$$

where: T_m is the melting temperature ($^{\circ}\text{C}$); T_c is the crystallization temperature ($^{\circ}\text{C}$); t is the time required to melt the specimen (min); R is the heating rate ($^{\circ}\text{C}/\text{min}$).

During crystallization many photomicrographs of the growing spherulites are taken, and the time is recorded for each photo. The slides were mounted in an increasing order on a slides holder. First, a projection of a scaled slide is measured to determine the conversion factor from millimeters to micrometers which depend on the magnification at which the photo was taken and on the distance of the projector to the wall. The diameter of the spherulites were measured in millimeters and then converted to micrometers by the conversion factor.

3.4 Wide Angle X-Ray

Wide angle x-ray diffraction, WAXD, studies were carried out using a Rigaku Denki diffractometer. Samples were isothermally prepared for SAXS and WAXD analysis in silicon oil bath.

3.5 Small Angle X-Ray Scattering

Small angle x-ray scattering, SAXS, studies were carried out at the Center for Small Angle Scattering Research at Oak Ridge National Laboratories using a sample to detector distance of 5m (Fig.3.5). The x-ray source is a rotating anode with $\text{CuK}\alpha$ ($1.54\text{\AA}$) wavelength. The sample thickness ranged from 1 to 1.5 mm.

Schematic representation of the SAXS experiment is shown in figure 3.5. The detector is a two-dimensional position sensitive proportional counter [138]. All samples were mounted on an aluminum wheel which is controlled with an automated motor, connected to the main computer. The data was collected with a high speed computer for one hour for each sample.

Data Correction

All data are corrected by subtracting the instrument background and the dark current. In separate runs, the instrument background and the dark current are collected under the same condition used for the samples. The dark

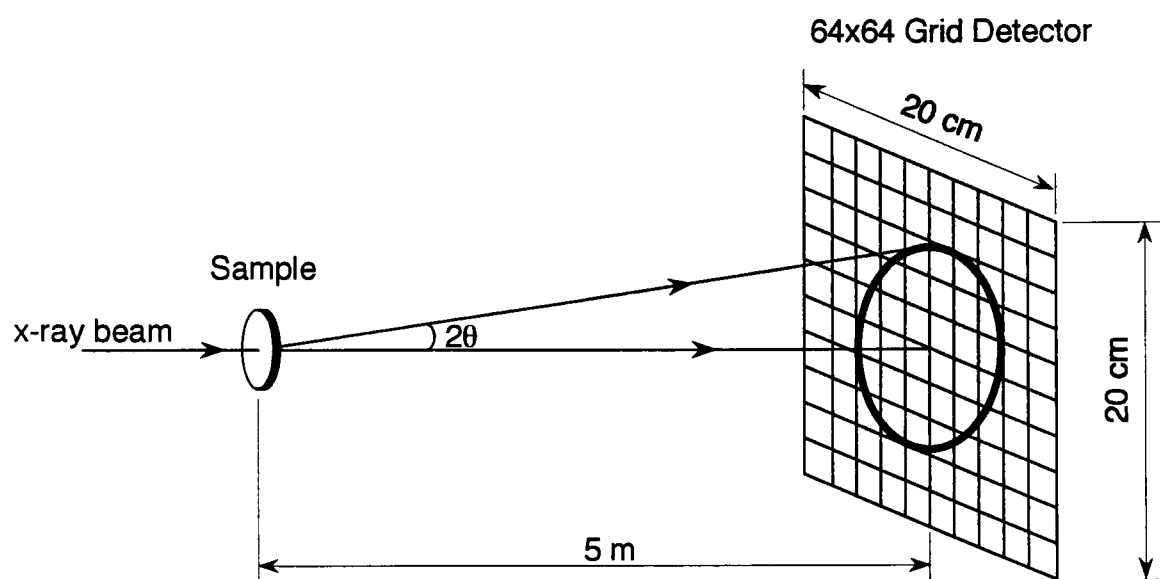


Fig.3.5 Schematic of SAXS experiment.

current run is done by blocking the beam path with lead sample. Thus, the collected data is due only to the radiation events which originate in cosmic radiation and electronic noise. The instrument backgrounds are collected with no sample in the beam. Finally, the net corrected scattering intensity, I_{corr} is defined as the following:

$$I_{\text{corr}} = \frac{1000}{\text{Mon}_s T_{m,s} \text{th } S_{i,j} F_{\text{abs}}} \left\{ \left[I_s - \frac{t_s}{t_{\text{DC}}} I_{\text{DC}} \right] - \frac{T_{m,s}}{T_{m,MT}} \left[\frac{\text{Mon}_s}{\text{Mon}_{MT}} I_{MT} - \frac{t_s}{t_{MT}} I_{\text{DC}} \right] \right\} \quad (4.1)$$

where:

Mon_s = monitor counts of sample scattering measurement.

Mon_{MT} = monitor counts of empty beam scattering measurement.

1000 = an arbitrary chosen normalization constant.

I_s = the scattering intensity measurement of the sample.

I_{MT} = the scattering intensity measurement of the empty beam.

t_s = time in seconds for sample scattering measurement.

t_{DC} = time in seconds for dark current measurement.

t_{MT} = time in seconds for empty beam measurement.

$T_{m,s}$ = transmission coefficient of sample.

$T_{m,MT}$ = transmission coefficient of empty beam.

t = sample thickness in mm.

$S_{i,j}$ = detector pixel sensitivity correction factor.

F_{abs} = absolute intensity conversion factor derived from standards

The sample transmission coefficient, T_m , is determined from preliminary studies of SAXS. For short runs (about 40 sec), the intensity of each sample is collected with and without glassy carbon. T_m is determined as follows:

$$T_m = \frac{(I_{gcs} - I_{DC}) - 0.686(I_s - I_{DC})}{(I_{gc} - I_{DC}) - 0.686(I_{MT} - I_{DC})} \quad (4.2)$$

where:

I_{gcs} = measured intensity of glassy carbon and sample.

I_{DC} = measured intensity of dark current.

I_s = measured intensity of sample alone.

I_{gc} = measured intensity of glass carbon.

I_{MT} = measured intensity of empty beam.

The sensitivity of the detector is determined by collecting data of a radioactive material such as iron-55 isotope.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Melting

4.1.1 Melting of iPP

Lamellar Thickness Studies

SAXS experiment and lamellar thickness Studies were conducted by R. A. Campbell, and the results are reported in his dissertation [10].

SAXS data were collected as two-dimensionally averaged scattering intensities. All specimens exhibited circularly shaped two-dimensional plots, indicative of isotropic materials. Figure 4.1 shows a plot of radially averaged intensity versus scattering vector for the polymer of 151K M_w as a function of isothermal crystallization temperature. As expected the peak shifts to lower q values as crystallization temperature increases, reflecting the increase in long period. In general, the curves show relatively well defined Bragg maxima. The curves were corrected using the Lorentz geometric factor, the corrected data being shown in figure 4.2. Corrected curves typically show a relatively sharp primary peak with occasionally a secondary peak of much lower intensity at higher scattering vector values.

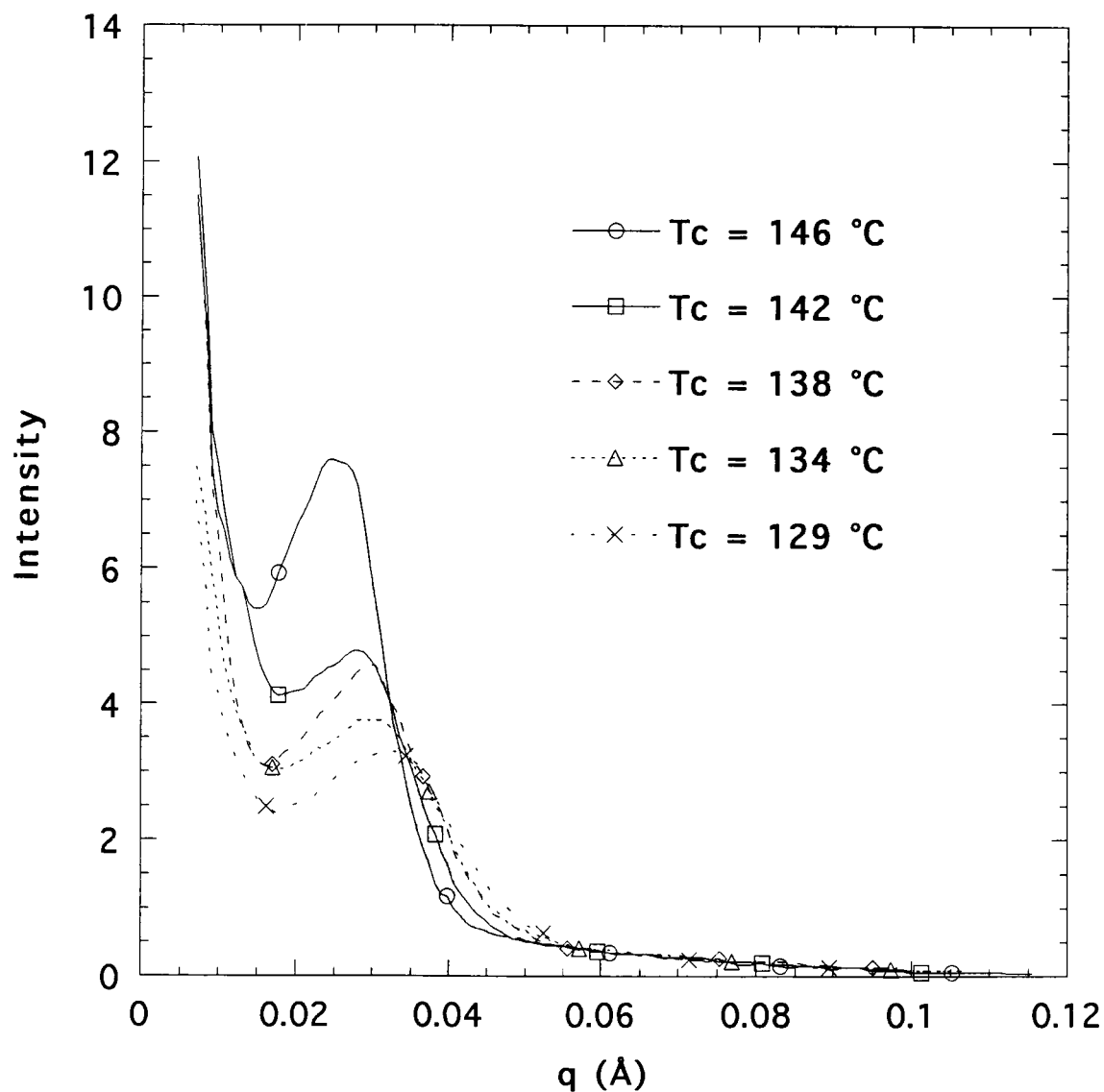


Fig.4.1 SAXS radially averaged intensity I versus scattering vector q for isotactic polypropylene $M_w=151k$ isothermally crystallized at atmospheric pressure and several crystallization temperatures.

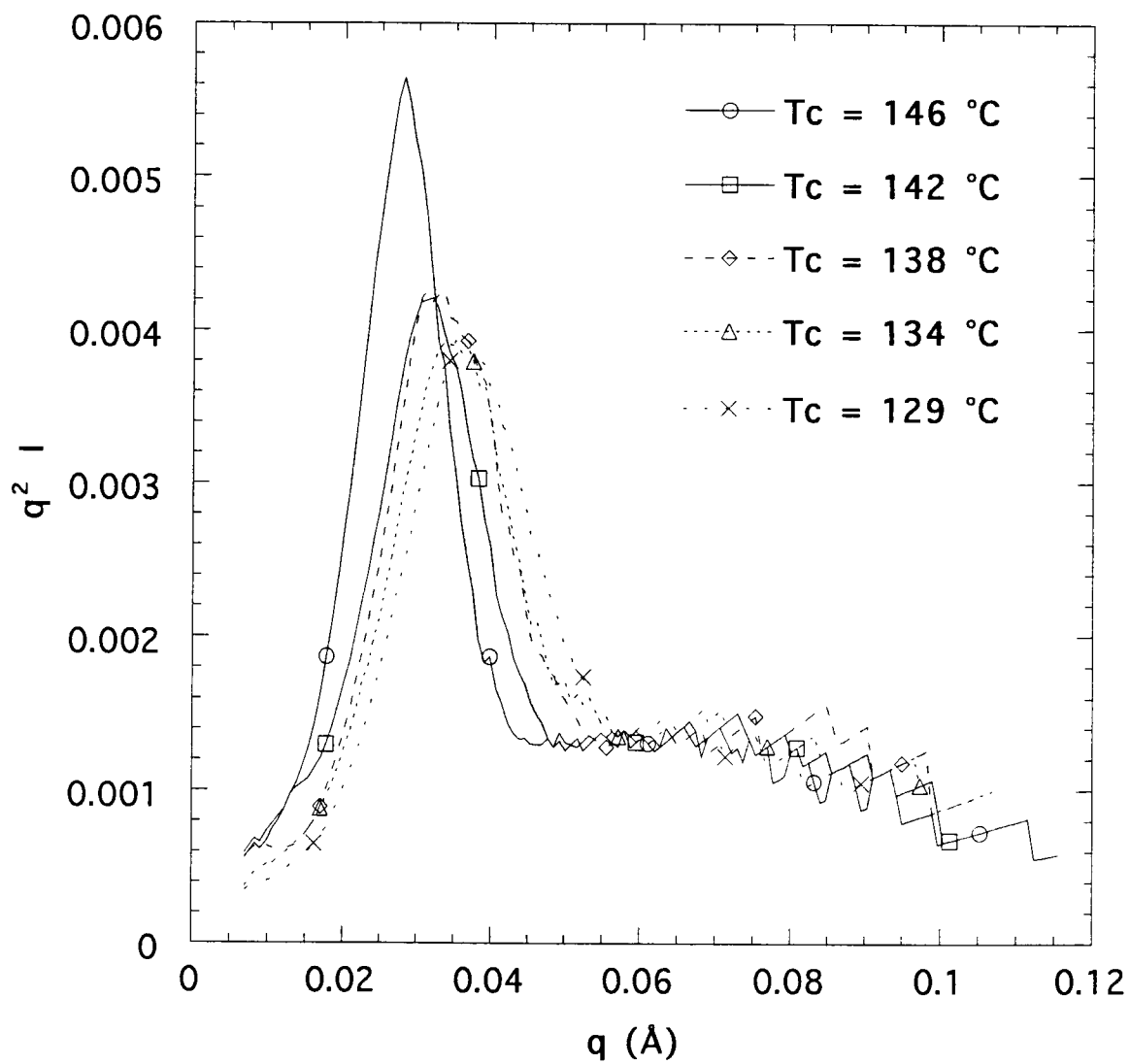


Fig.4.2 SAXS Lorentz corrected plots for the data of Fig.4.1.

More detailed analysis of SAXS data can be made by performing distance distribution function ($\rho(r)$) and electron density correlation function ($\gamma(r)$) plots. The distance distribution plot gives information on the nature of the scattering. Such analyses (Fig.4.3) indicate a concentrated system in that a minimum occurs with negative values of the distance distribution. Data for other crystallization temperatures were similar.

A representative electron density correlation function plot is shown in Fig.4.4 and is typical of a two plane system with long period variation, lamellar thickness variation and a diffuse phase boundary. The data are consistent with literature results for other semi-crystalline polymers^[127]. The long period determined from such a plot was found to be larger than those determined from the observed SAXS intensity profiles. Table 4.1 gives the details of long periods determined from obtained SAXS intensities, Lorentz corrected intensities, and from electron density correlation function with crystallization temperature.

A plot of melting point versus reciprocal lamellar thickness is shown in Fig.4.5. Lamellar thicknesses were estimated using the traditional method of multiplying the long period by crystallinity determined from WAXD. The melting points used here were determined from direct optical

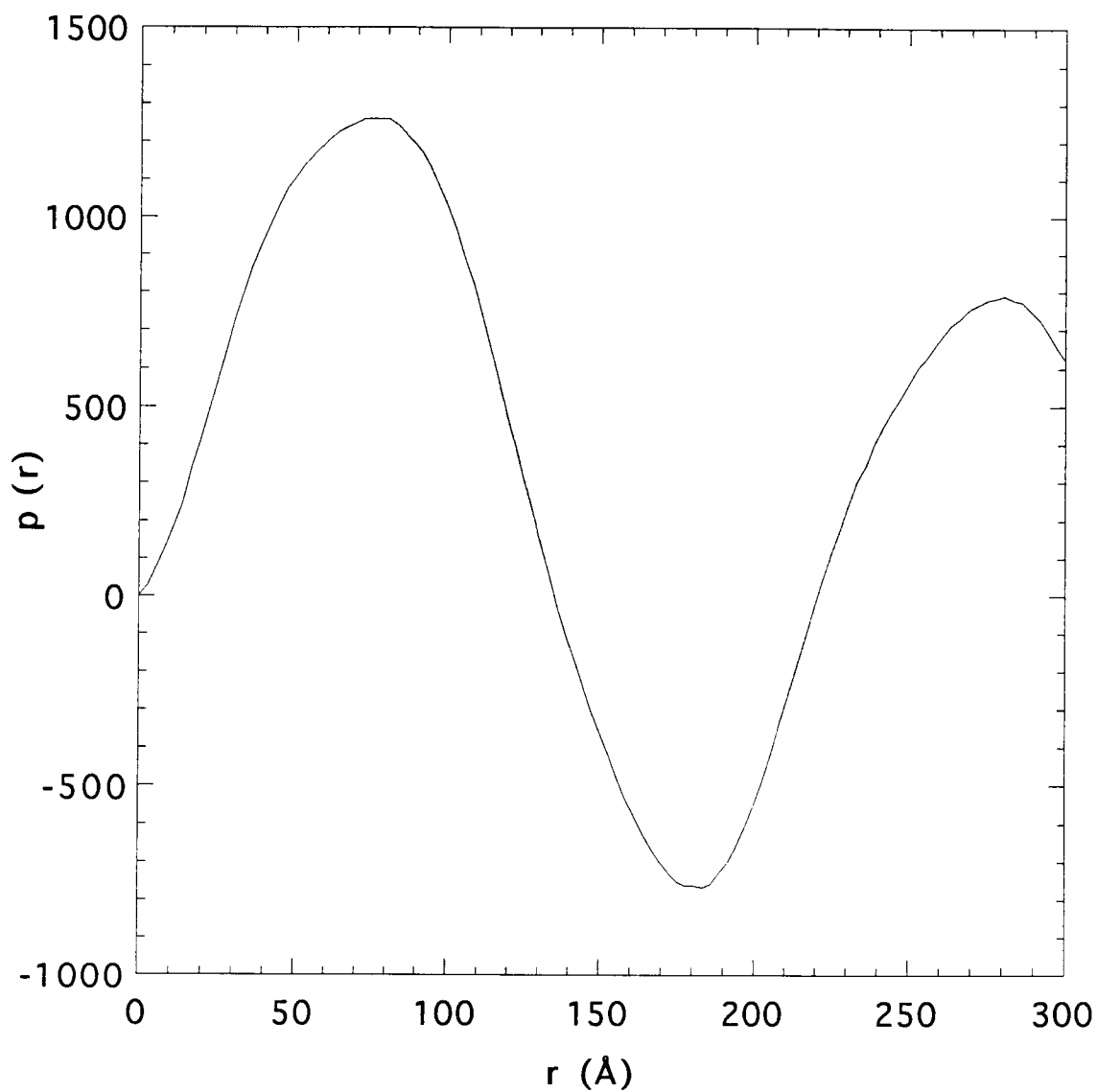


Fig.4.3 Distance distribution function, $p(r)$, for isotactic PP isothermally crystallized at $\Delta T=47^\circ\text{C}$. SAXS intensity profile recorded at 25°C .

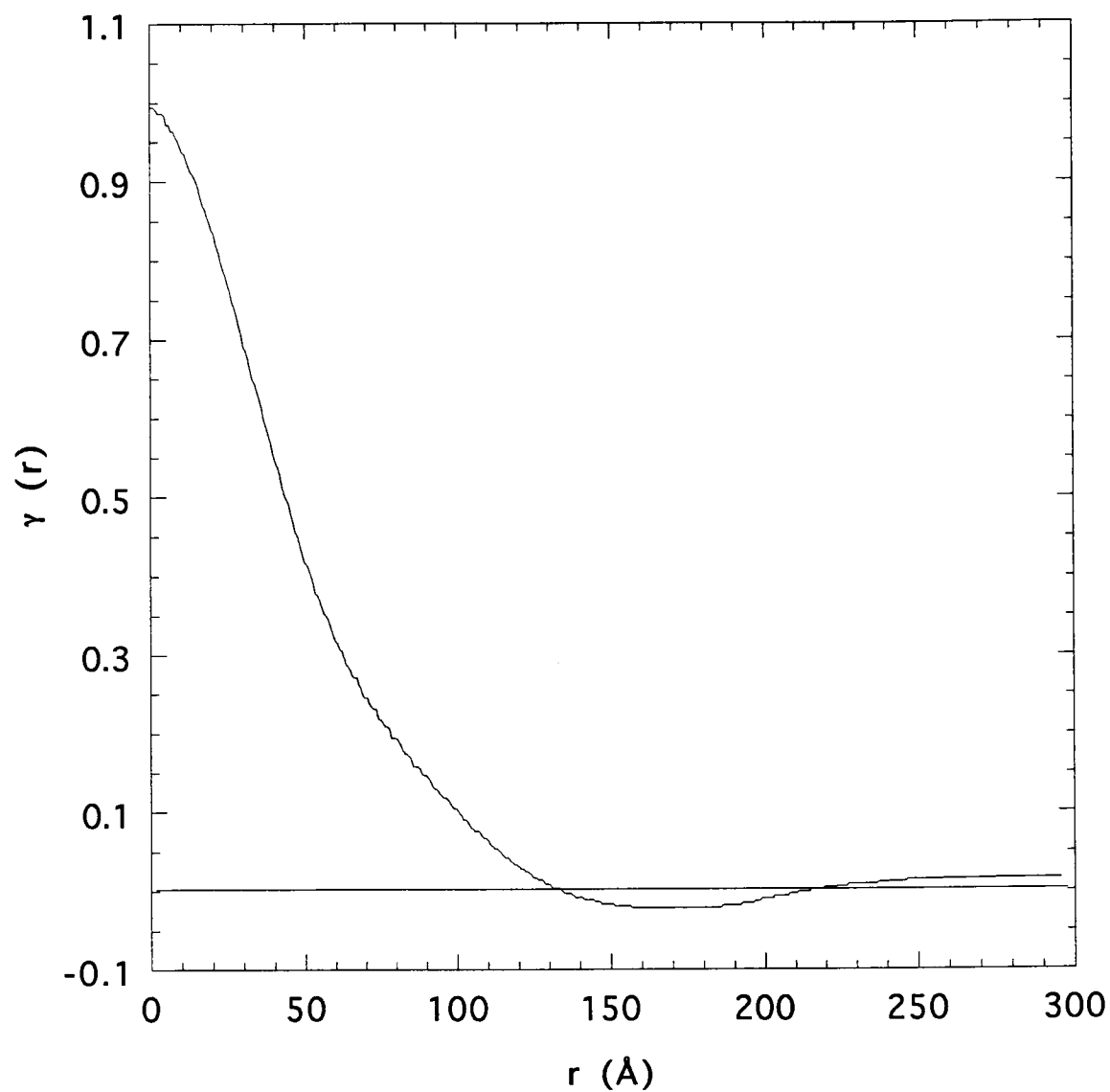


Fig.4.4 Electron density correlation function, $\gamma(r)$, for isotactic PP isothermally crystallized at $\Delta T=47^\circ\text{C}$. SAXS intensity profile recorded at 25°C .

Table 4.1: Comparison of long periods determined from SAXS, observed intensity and electron density correlation functions.

T_c	$L, \text{ \AA (Bragg)}$		$L (\gamma)$
	LC	Obs	
127	184	218	221
129	192	226	226
134	198	248	236
136	210	238	252
137	210	238	266
138	208	248	262
139	210	256	266
140	226	248	267
141	224	256	271
142	230	256	281
143	230	276	256
144	238	276	261
146	248	298	303

- * T_c is the crystallization temperature ($^{\circ}\text{C}$)
- * LC Lorentz corrected lamellar thickness from q - q^2I data
- * Obs is the observed lamellar thickness from q - I data
- * $L (\gamma)$ is the lamellar thickness from correlation function γ

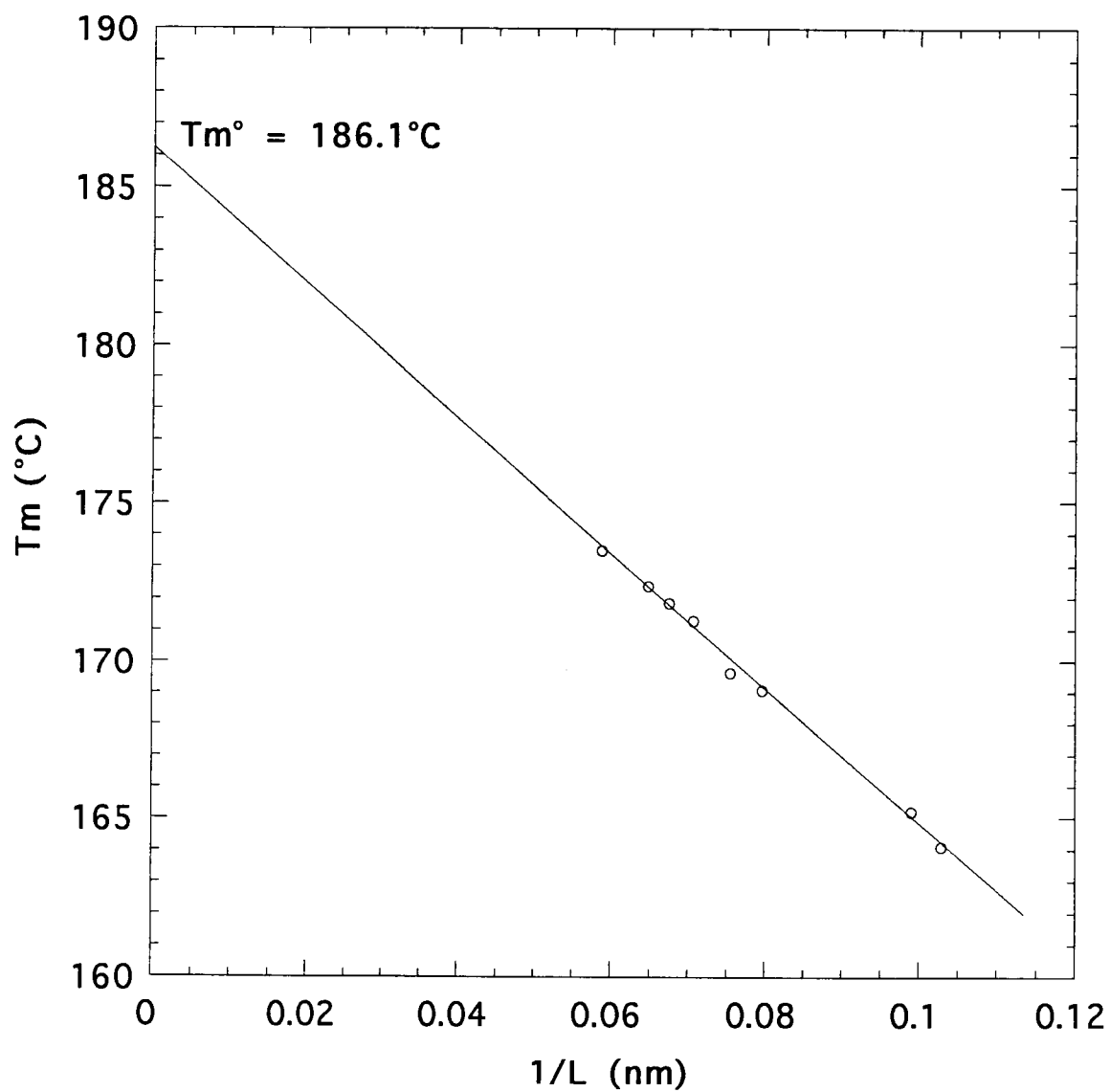


Fig.4.5 Melting temperature, T_m , from DLM of iPP ($M_w=151K$) versus reciprocal lamellar thickness from SAXS using Lorentz corrected data.

microscopy in a hot stage at 10°C/min after long crystallization time, which will be discussed in the next section.

Dynamic Light Intensity

The melting behavior of α -spherulites of polypropylene is complicated by the presence of thin lamellar branches inclined at 80° to the dominant radial lamellae [37,38,43,46,48,70]. Their angle of inclination leads to a partial compensation of the birefringence arising from the radial lamellae. This effect is responsible for the well-known low birefringence of α -spherulites. 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 (Fig.4.6a). 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. As a function of the time of crystallization, the temperature at which zero birefringence is attained can be seen to increase (Fig.4.6a). The latter effect is caused by the lamellar thickening of the radial lamellae and for the example shown in Fig.4.6a of 140°C crystallization there is a difference of 1.5°C in this value between half an hour and 14 hours of crystallization time (Fig.4.6b). This effect can be observed over much of the crystallization range. The amount

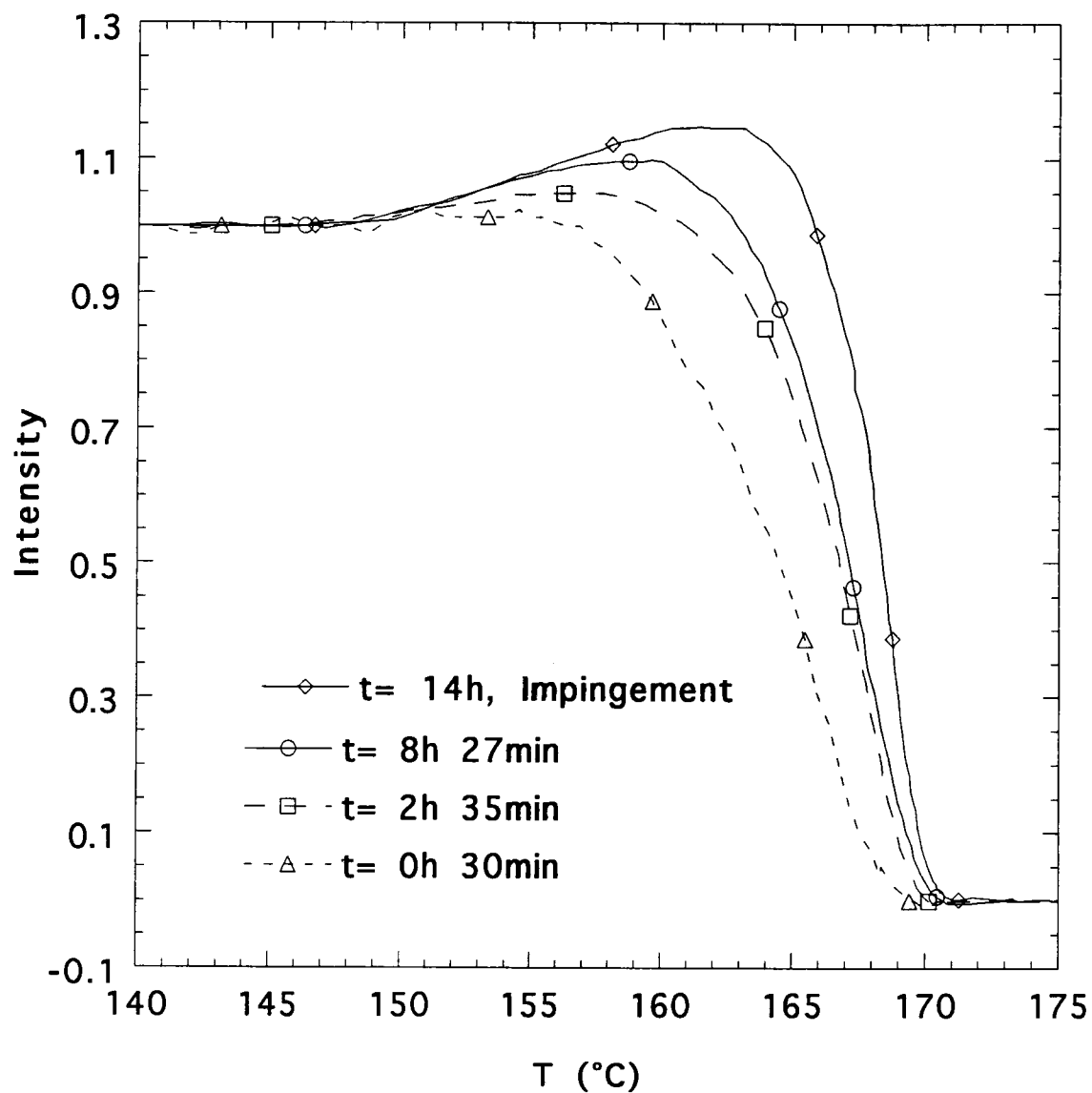


Fig.4.6: Light Intensity, I , versus temperature, T , for different crystallization times, t , at 140°C . Heating rate is $10^{\circ}\text{C}/\text{min}$.
a) Entire melting range.

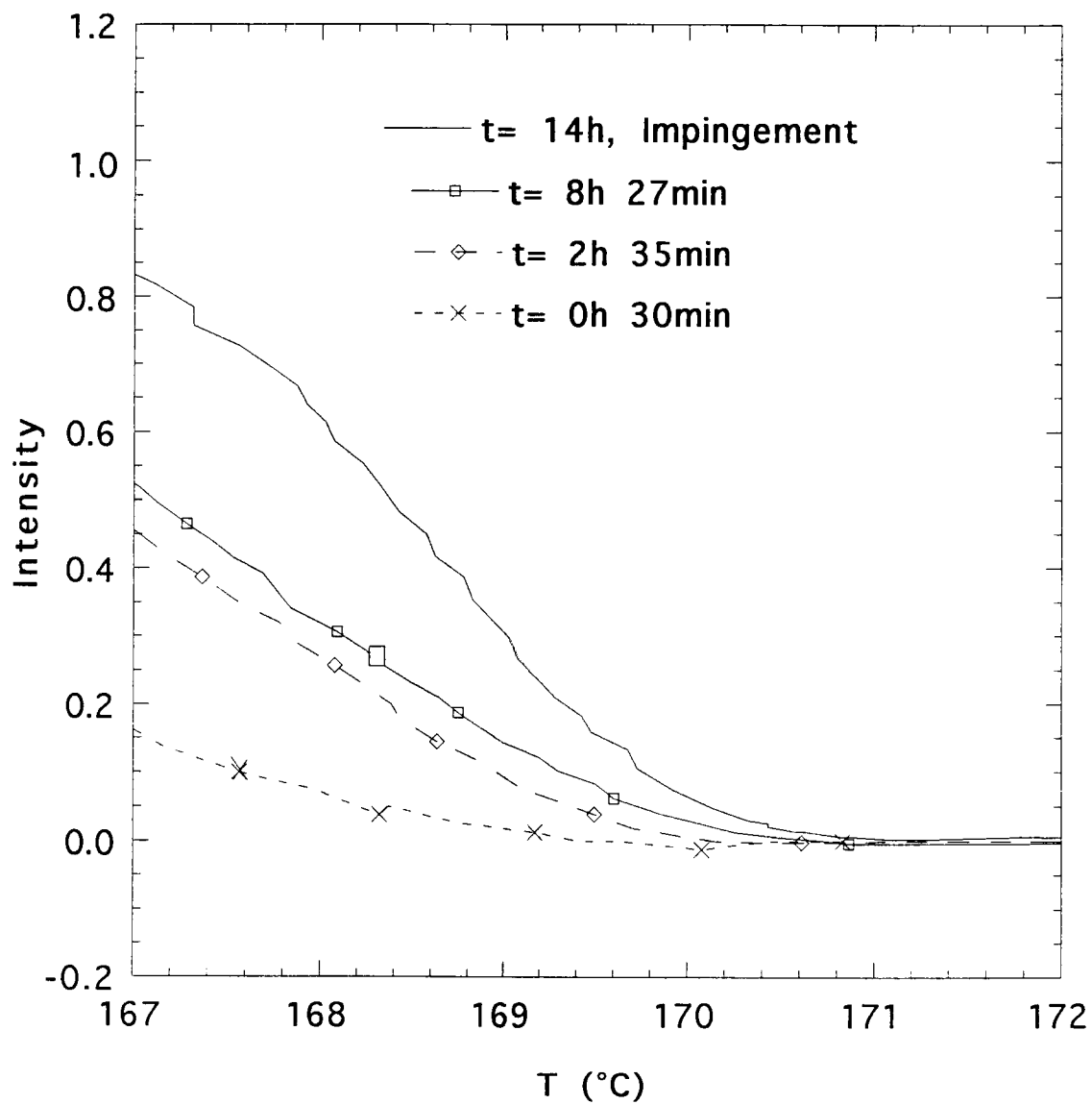


Fig.4.6 (continued): b) Magnification of the end of melting region of Fig.4.6 a). The melting point after 14h is 1.5°C higher than after 30 min.

of thickening being greater at low supercoolings, due to the long crystallization times necessary for production of a specimen, has an unduly large effect on extrapolations of equilibrium melting point.

Clearly this effect will confuse traditional extrapolations as illustrated in Fig.4.7, where two extrapolations are performed. First, specimens have been crystallized for long times and at least to impingement. The points fall reasonably well on the drawn line which is the best fit line for the data points. It can be seen that the extrapolation leads to an equilibrium melting point close to 210°C . Secondly, specimens were crystallized for very short times and then the melting points determined. In this case it was necessary to allow sufficient crystallization for an accurately measurable light intensity trace to be obtained. Obviously the transmitted intensity is proportional to the crystallinity in the sample and a certain minimum crystallinity was necessary in each case. When plotted, the points give the best fit line shown and an extrapolated equilibrium melting point of 188.8°C . The equilibrium melting temperature would be more accurate if one could measure the melting temperature characteristic of newly initiated spherulites, but this is very difficult using current instrumentation. The first difficulty encountered is the sensitivity of the light intensity detector. The second

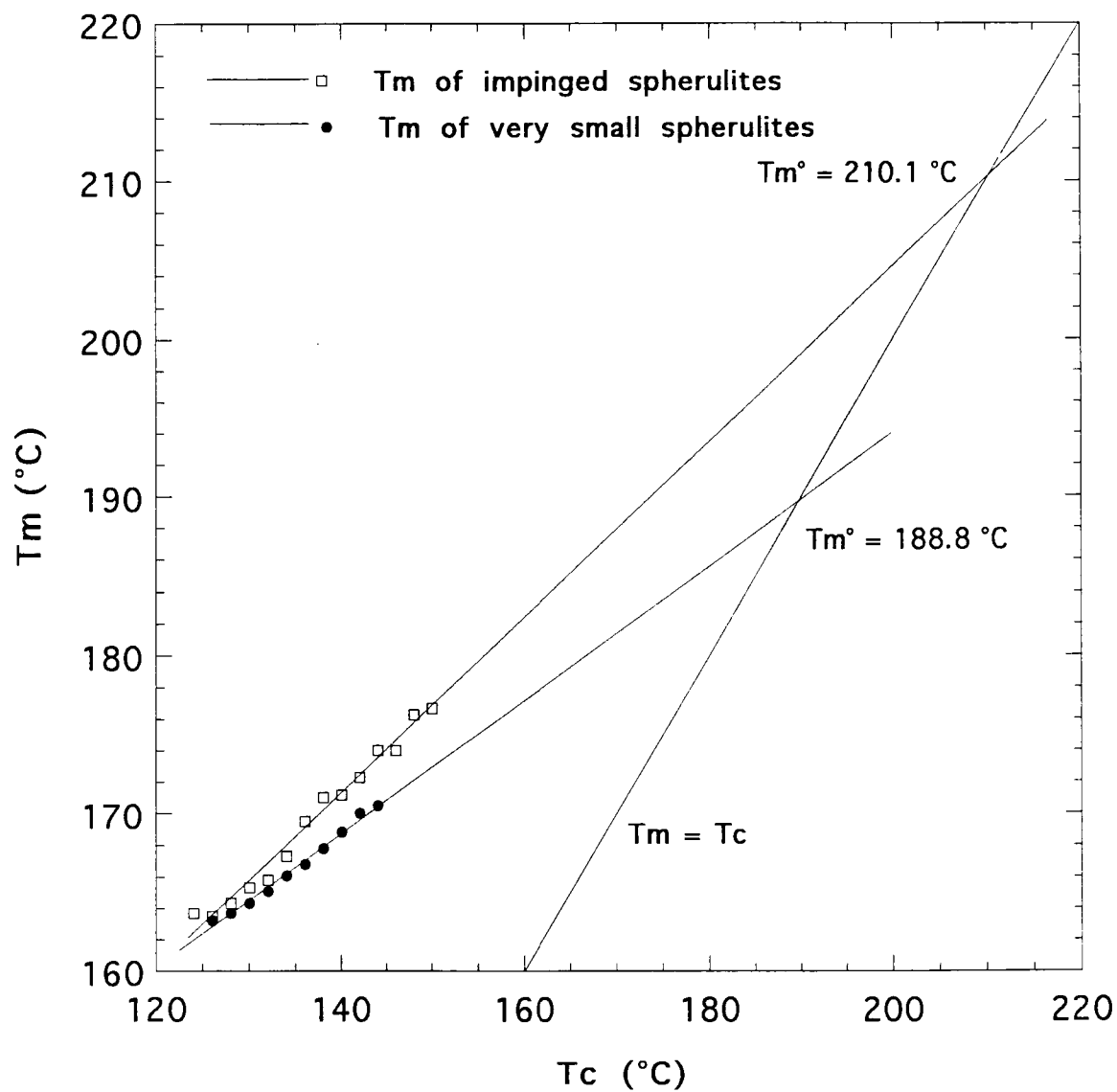


Fig.4.7 T_m versus T_c for two experiments that yield distinct equilibrium melting temperatures, T_m° . The experiments differ only in crystallization time.

problem is the continuous crystallization of the polymer that occurs during heating at a moderate rate such as 10°C/min from low crystallization temperatures. This effect is manifest in the formation of rings that grow at the edge of spherulites during heating of the specimen (Fig.4.8). Both of these problems are not easily overcome. Also in Fig.4.8 one can see the melting of small spherulite (arrow) preceding the melting of a large one.

When specimens were crystallized for very short times T_m^0 was determined to be 184.5°C (Fig.4.9) from the peak temperatures using the DSC instrument. The melting points shown in Fig.4.9 are the peaks of each plot given by the DSC. The peak represents the average melting point compensated by the distribution of spherulite sizes and, hence, lamellar thicknesses. Also, the melting of thin lamellar branches and the rings which were formed during melting were included in the peak measurements. The modified return-to-the-baseline measured the melting point of the rings that developed during heating at 10°C/min. Such rings were only formed when the isothermal crystallization was below 135°C. When crystallized at high temperatures (Fig.4.10) the rings did not form and the return-to-the-baseline temperature could be extrapolated accurately to give an equilibrium melting point close to 186°C.

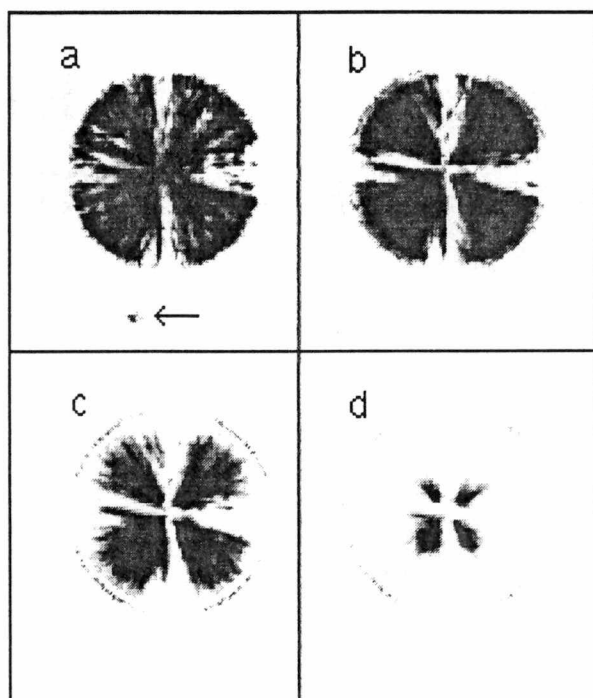


Fig.4.8 Typical melting of iPP spherulites crystallized below 135°C and heated at 10°C/min. a: crystallized spherulite ($T_c = 135$ for 52 min.). b, c, and d: during melting after 3 min. 2 sec., 3 min. 8 sec., and 3 min. 14 sec., respectively. Notice the appearance of the ring and the radially melting. Also notice that from a to b the small spherulite (arrow) has melted.

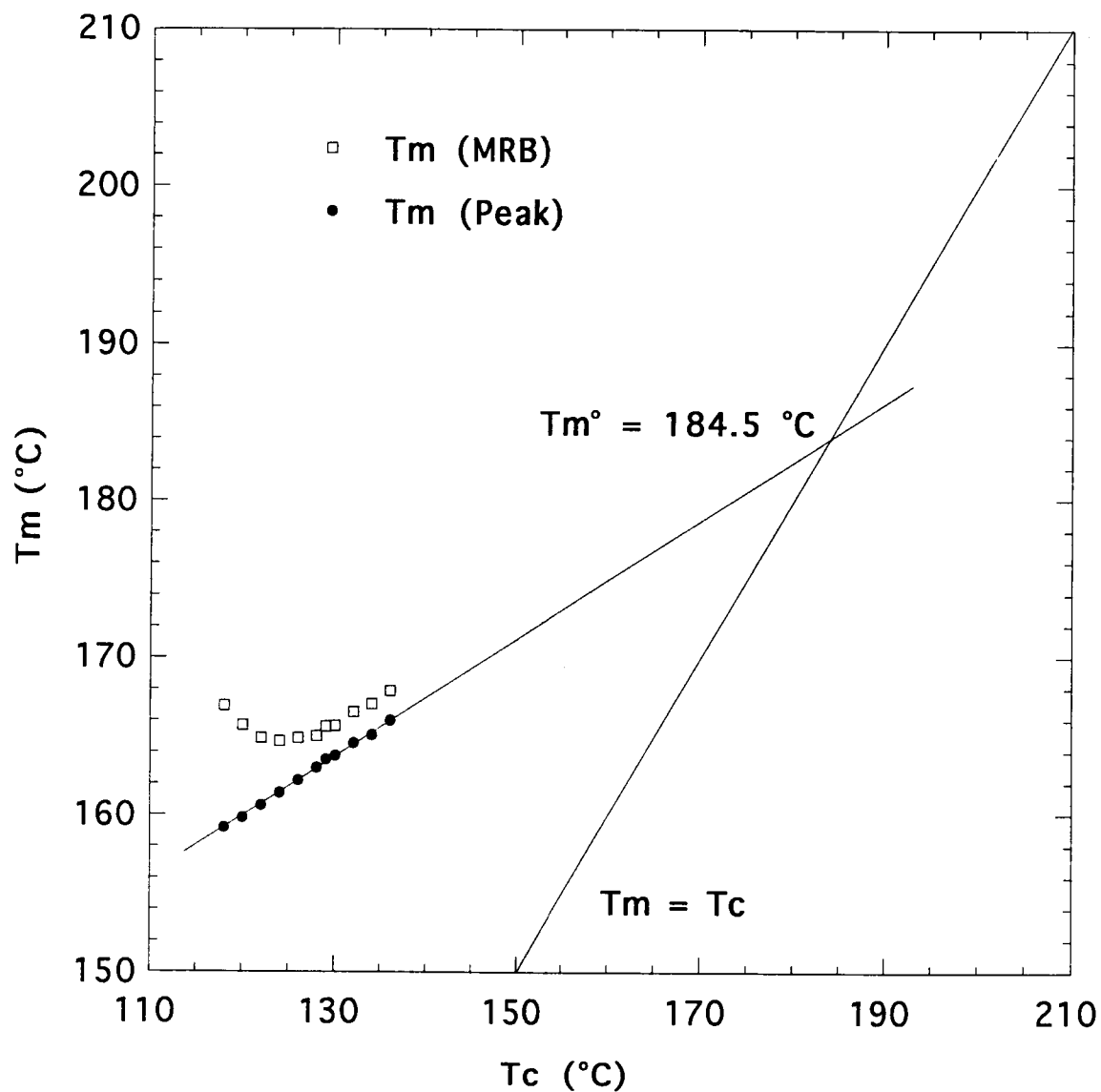


Fig.4.9 T_m versus T_c , using the peak and The modified return-to-the-baseline (MRB) temperatures from DSC. The data were collected after a short time of crystallization.

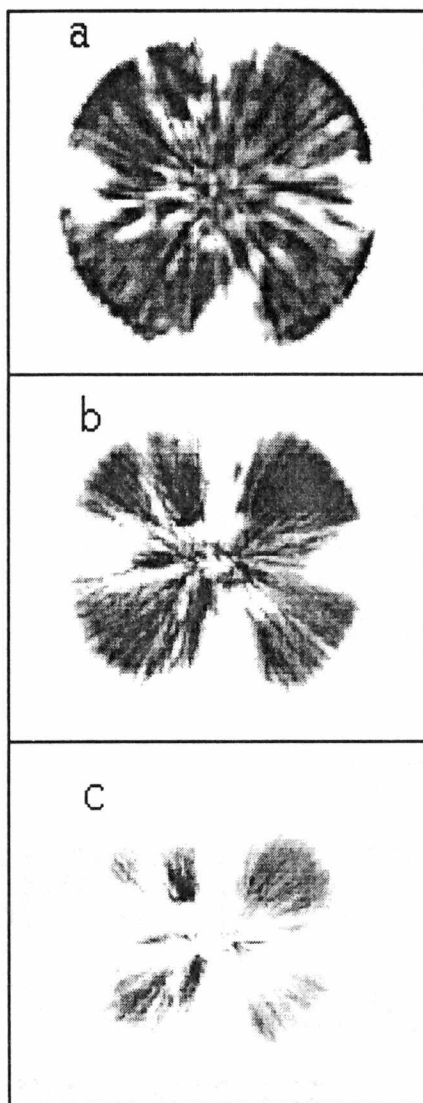


Fig.4.10 Typical melting of iPP spherulites which crystallized above 140°C and heated at $10^{\circ}\text{C}/\text{min}$. a: crystallized spherulite ($T_c = 150$). b, c, and d close to melting. Notice that no ring appears during melting and the spherulite radially melts toward its center.

Although the Hoffman-Weeks' plot used is very convenient for equilibrium melting point determinations, it was never claimed that it was a substitute for the primary extrapolation, which must involve an extrapolation of melting point versus lamellar thickness. The latter process is much more lengthy and requires accurate determinations of lamellar thicknesses and crystallinities. This usually entails the use of both small angle and wide angle x-ray studies. When such determinations are conducted for polypropylene (Fig.4.5) they result in an extrapolation which, when best fit, generates an equilibrium melting point of 186.1°C , which correlates well with the lower value obtained from Hoffman-Weeks' plots.

The value of the equilibrium melting point of polypropylene is therefore believed to be close to 186°C . A more precise evaluation is not easily possible because of the inherent errors in all of the techniques which have to be used. Analyses reported in the literature of the kinetics of crystallization of polypropylene using an equilibrium melting point of 210°C or above (e.g., ref. 4 and 74) need to be reevaluated. The extrapolations producing the equilibrium melting point of 210°C have all been carried out using established techniques and have been conducted in an acceptable manner. Why then is it so different from the value obtained using small angle x-ray scattering? The answer lies in the nature of the self-annealing mechanism occurring at

the crystallization temperature. Most studies of self-annealing have considered polyethylene and generally at low supercoolings. The clearly recognized dependence on annealing is that the slope of a curve of melting point versus crystallization temperature is decreased.

In the study reported here the slope clearly increased when long crystallization times were used instead of short ones. However, the crystals produced at the highest supercooling showed only marginal increases in melting point with time. In other words their thickening process was being inhibited. Crystals produced at low supercooling showed the largest increases in melting point. Furthermore, the line fits for the curves of Fig.4.7 clearly indicate that the inhibition of the thickening process is dependent on temperature in a somewhat linear fashion. The curve for impinged spherulites is fairly straight above 135°C but has a much lower slope below that temperature. Indeed, it is relatively close to that for the newly formed spherulites. However, natural scatter of the data prevents any stronger statements from being made, although it is noted that 135°C is close to the Regime II- Regime III transition temperature.

The results of the study raise some fairly serious questions regarding the current level of understanding of lamellar thickening processes. First, it has generally been assumed that the thickening coefficient is a constant value

resulting in the melting points of the thinnest crystals being affected the most by an annealing process because they are far from equilibrium dimensions. However, here there is a clear example of the thicker crystals being affected most by the thickening process. It should also be recalled that in earlier studies of poly(ϵ -caprolactone)s [22] that the thickest crystals tended to be able to approach equilibrium more easily than thinner crystals. In this case it was assumed that the low molecular weight of the polymer enabled thicknesses approaching complete extension to be reached easily.

The mechanism of thickening must involve a snaking through the crystal of lengths of chain. It is a reasonable assumption that the activation energy of the snaking process should be proportional in some way to the thickness of the crystal because of the length of chain involved dictating the total amount of internal frictional resistance encountered. The results presented here conflict with such a reasonable assumption. Such a model does not allow for the impediment to thickening caused by the presence of some non-adjacent reentry folding, nor does it consider the influence of tie-molecules. Analyses of the crystallization kinetics of polypropylene at atmospheric pressure show that the commonly-encountered high molecular weight polymer crystallizes in Regimes II and III dependent on temperature [9,25]. Regime

theory states very explicitly that a change of regime does not interfere with the expected linear dependence of the unthickened lamellar thickness on supercooling. All the experimentation carried out to date on several polymers confirms this conclusion. Regime theory does not deal with any thickening process, but it is possible to infer some reasonable hypotheses regarding the nature of the folded surface and how it varies with regime.

Although some might dispute this statement, it has been generally assumed that Regime I conforms most closely to the adjacent reentry surface. In Regimes II and III, in which there is multiple nucleation, there is a tendency to incorporate more non-adjacently reentered stems into the surface as well as increasingly larger numbers of non-reentered molecules. This tendency tends to be favored as the supercooling is increased and hence should be greatest in regime III. The type of disordered surface generated is sometimes referred to as an interfacial layer [139]. In any case, disrupting the continuity of adjacent reentry has to present a major obstruction to the lamellar thickening process. It should render the thinner lamellae produced at high supercooling incapable of responding adequately to the thermodynamic driving force for thickening. The data in the literature on thickening of polyethylene crystals considers largely crystals generated under Regime I conditions where

adjacent reentry dominates the crystallization process. It is therefore suggested that the thickening behavior exemplified by polyethylene crystallized at low supercoolings, and characterized by a lower slope to a plot of T_m versus T_c , should not be taken as representative of all polymers, but may be typical only of polymers crystallized under Regime I conditions where adjacent reentry predominates.

It is remarkable that the break in the T_m versus T_c curve for the impinged spherulites occurs at 135°C. This value is close to the Regime II - Regime III transition temperature of 138°C. Remembering that the data reported have excluded specimens in which crystallization might have occurred prior to reaching the crystallization temperature, it would be reasonable to suggest that the lowest slope demonstrating little or no thickening is characteristic of Regime III crystals. The curve giving rise to the slope that generates a T_m^0 of 210°C is then characteristic of Regime II growth. It therefore appears that lamellar thickening in Regime II is characterized by a temperature dependent thickening coefficient. It is very tempting to suggest that this is giving a measure of the fraction of adjacent reentry folding present in the surfaces, but such a speculation would be virtually impossible to test.

It is possible that a reevaluation of literature data will support the mechanism as being common to many polymers.

Most studies show a low or zero slope region at high supercoolings which has been ascribed to non-isothermal crystallization and ignored. Following on the suggestion of the existence of regime transitions, a reevaluation of kinetic analyses proved to be very valuable. Perhaps a similar reevaluation of Hoffman-Weeks plots would be in order.

4.1.2 Melting of Deuterated iPP

The equilibrium melting temperature, T_m° , of polypropylene was discussed in a previous section involving lamellar thickness studies, in which it was demonstrated that the correct value is 186.1°C. It was also demonstrated that polypropylene has a peculiar lamellar thickening process which results in abnormally high estimates of T_m° if long crystallization times are used. In the case of deuterated polypropylene it is anticipated that a similar problem exists and so short crystallization times are used in the procedure to be discussed. The results that were determined by DSC and DLM experiments are summarized in Fig.4.11 and Fig.4.12 respectively. According to figure 4.11, the equilibrium melting temperatures of iPPH and iPPD are determined to be 185.5°C and 177.2°C, which result in a difference of 8.3°C. Figure 4.12 represents the DLM results which yield two distinct equilibrium melting temperatures; 184.7°C for iPPH and 175.8°C for iPPD, and a difference of 8.9°C.

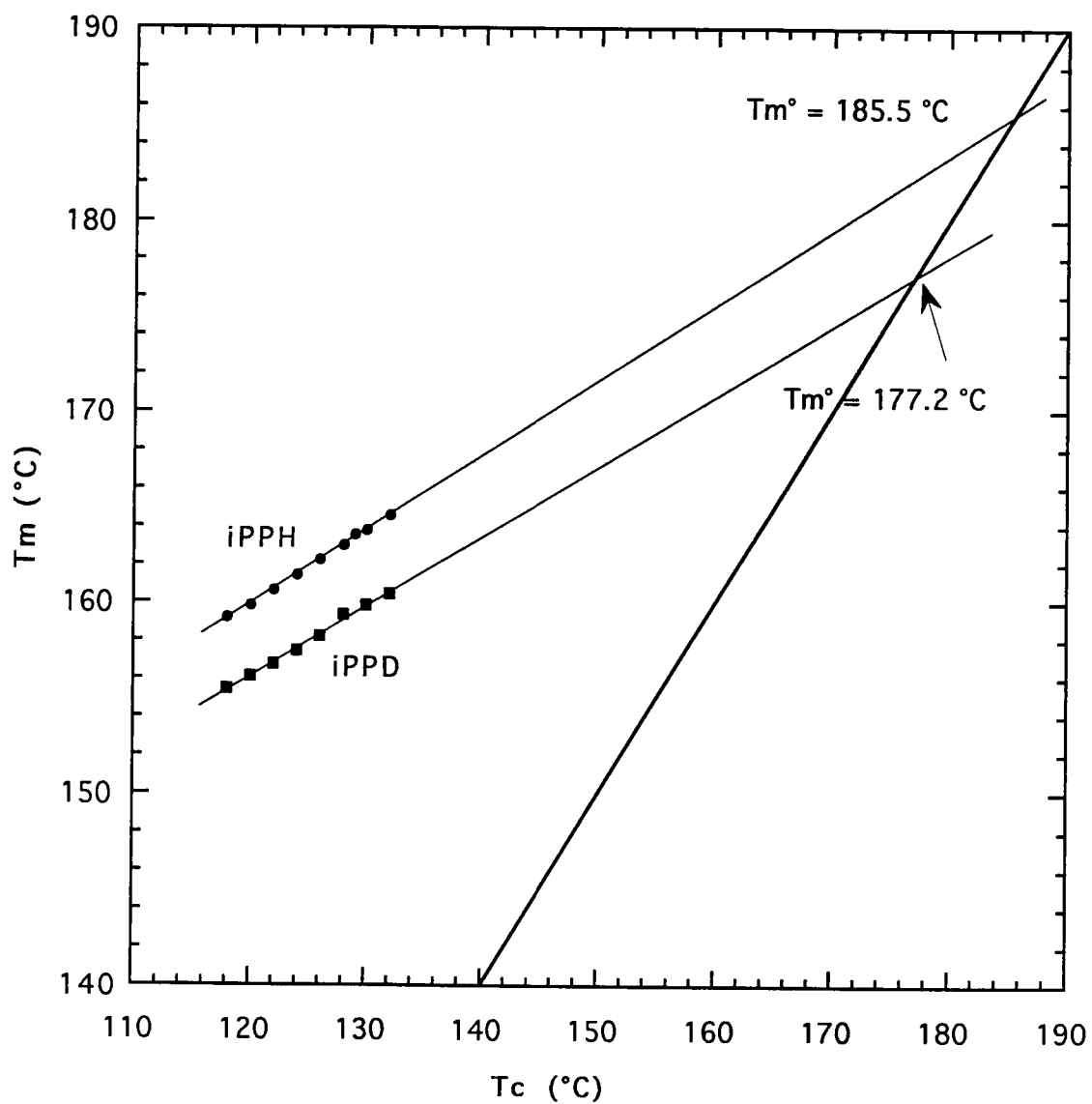


Fig.4.11 Equilibrium melting temperature, T_m° , of iPPH and iPPD using DSC peak temperature.

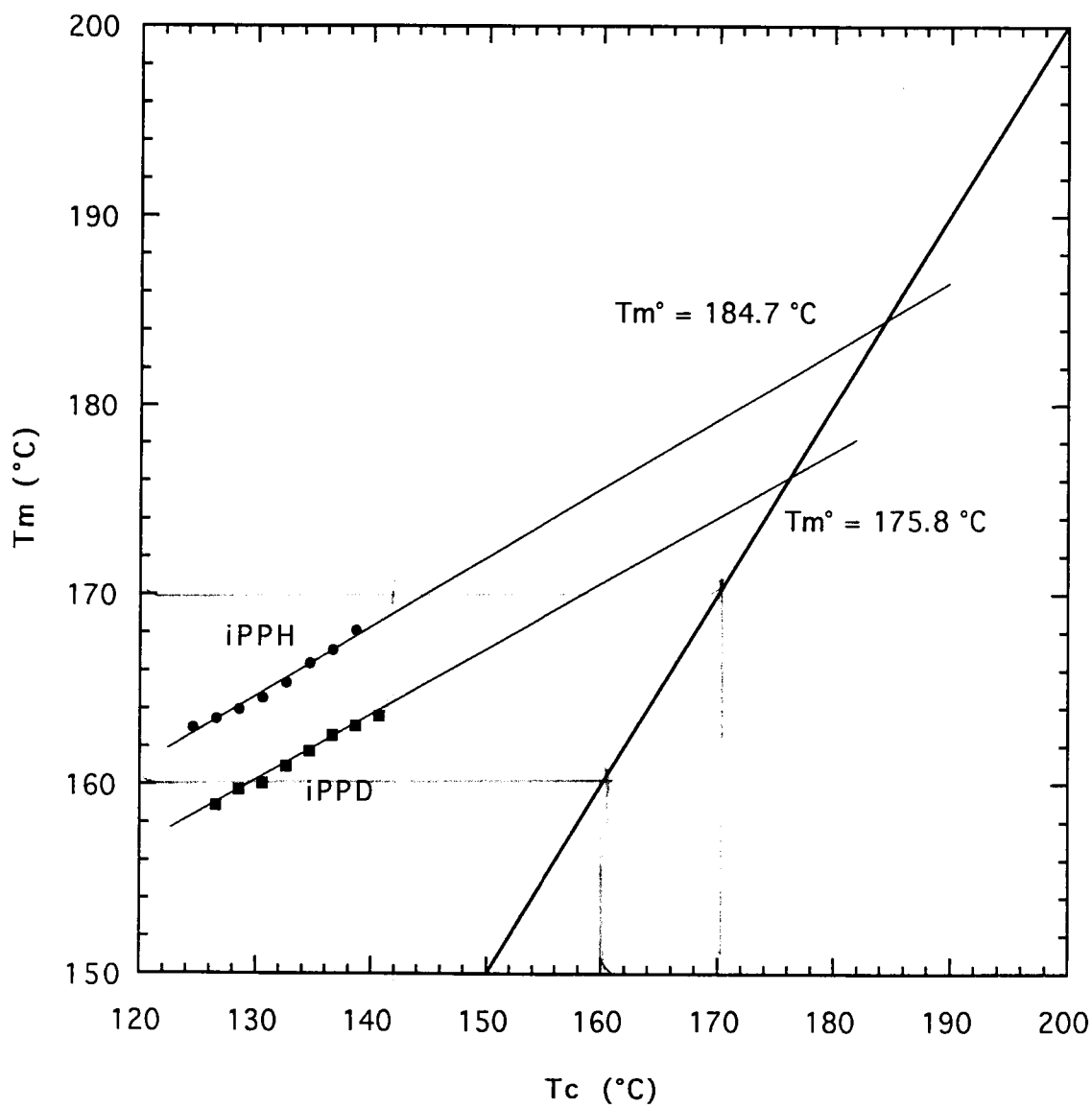


Fig.4.12 Equilibrium melting temperature, T_m° , of iPPH and iPPD using DLM experimental results.

As argued in the previous section, the accurate value of T_m^o can only be determined by measuring the lamellar thickness as a function of melting temperature. This measurement can be done by using both SAXS and WAXS. But, this procedure is very long and requires large amounts of material, which is not possible in the case of iPPD because of the high cost of the raw material.

Using x-ray experimentation, Bates et al. [17] have shown that substitution of deuterium for hydrogen results in a slight reduction in the parameters a and b of the unit cell of $C_{36}H_{74}$. This change is believed to be the result of a reduction in C-H bond length with deuterium substitution. In fact the C-D bond is $0.005\text{\AA}$ lower than the C-H bond. This reduction is manifest as a decrease in molar volume and polarizability.

As described by Bates et al. [17], the equilibrium melting temperatures of iPPH and iPPD can be correlated to the molar volume and polarizability as follow:

$$\frac{T_{mH}^o}{T_{mD}^o} \cong \left[\frac{\alpha_H}{\alpha_D} \frac{V_D}{V_H} \right]^2 \quad (4.1)$$

where α and V represent bond polarizability and molar volume of a polymer, respectively. H and D indices are symbols for iPPH and iPPD polymers. The values of T_m^o are in Kelvin.

Perdeuteration leads to a slight reduction in molar volume [140]. Based on the assumption that the *c* unit cell parameter is unaffected by isotope substitution the estimation of $V_H/V_D = 1.0014$ results only from the change in bond length with deuterium substitution in iPP [17]. The ratio $\alpha_H/\alpha_D = 1.0110$ is calculated from the polarizability change [17,132]. Using these values equation 4.1 yields:

$$\frac{T_{mH}^{\circ}}{T_{mD}^{\circ}} = \left[\frac{1.0110}{1.0014} \right]^2 = 1.0193 \quad (4.2)$$

$$\text{This implies that: } T_{mH}^{\circ} - T_{mD}^{\circ} = 0.0189 T_{mH}^{\circ} \quad (4.3)$$

Therefore, theoretically if $T_{mH}^{\circ} = 186.1^{\circ}\text{C}$, the difference in equilibrium melting temperatures is 8.7°C and $T_{mD}^{\circ} = 177.4^{\circ}\text{C}$. The experimental differences are 8.3°C and 8.9°C for DSC and DLM determination respectively (Table 4.2). The correlation between theory and experiment is therefore very strong for polypropylene.

The principle of this theory is based on the assumption that the entropy of fusion is dominated by an isotope independent conformational entropy and that the crystal structure remains unaffected by isotopic substitution. Using neutron scattering results, Stamm [15] has confirmed that both iPPH and iPPD have the same crystal structure.

**Table 4.2: Experimental and calculated values
of $(T_{mH}^{\circ} - T_{mD}^{\circ})$**

Experiment	T_{mH}° (°C)	T_{mD}° (°C)	Experimental $T_{mH}^{\circ} - T_{mD}^{\circ}$	Calculated $T_{mH}^{\circ} - T_{mD}^{\circ}$
DSC	185.5	177.2	8.3	8.7
DLM	184.7	175.8	8.9	8.7

4.2 Crystallization

4.2.1 Secondary Nucleation Analysis

Examples of the change in spherulite radius with time for selected temperatures are shown in Fig.4.13 and Fig.4.14, where it can be seen that linear growth rates result. Plots of growth rate versus temperature for both iPPD and iPPH can be seen in Fig.4.15 where it is clear that the rate of growth at any chosen temperature is lower for iPPD. When the data are analyzed using the Lauritzen-Hoffman equation, Fig.4.16, it is seen that both polymers show the Regime II- Regime III transition, previously identified for iPPH by several groups of workers [4,15,24,25]. In these analyses the values of T_m^0 used were 186.1°C for iPPH and 177.4°C for iPPD. It is found that when they are expressed in Kelvin the value of T_g is generally between 0.5 and 0.8 T_m^0 . If it is assumed that the same relationship exists between T_g and T_m^0 for both polymers (iPPH and iPPD) then $T_g = 0.57 T_m^0$. Values of U^* of 1500 cal/mol were used in each case, and glass transition values of -12°C for iPPH and -16.5°C for iPPD. It can be seen from Fig.4.16 that the transition in iPPH is sharper, but the data for iPPD are more extensive.

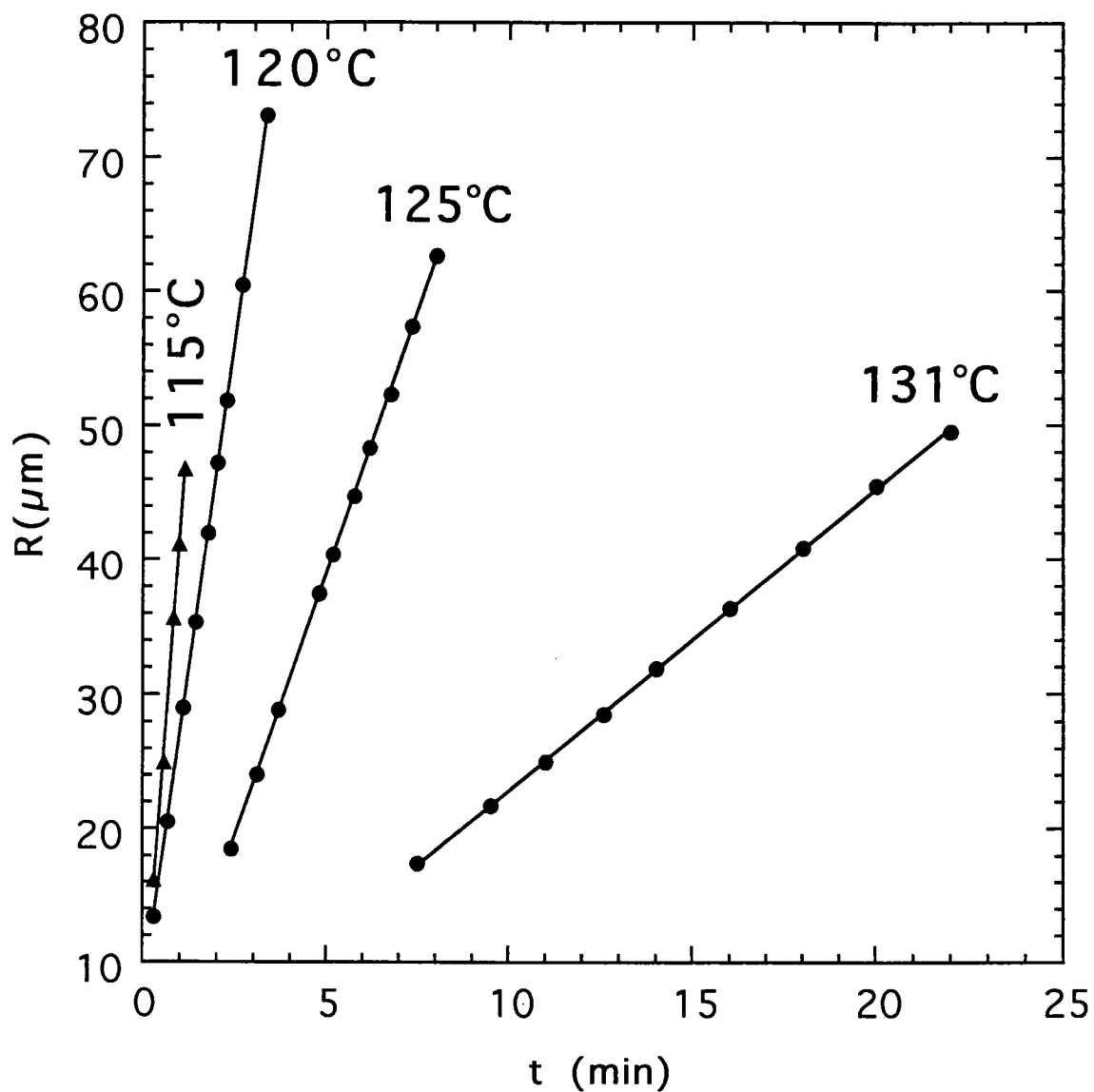


Fig.4.13 Spherulitic growth of iPPD for selected temperatures (115, 120, 125, and 131°C). The growth rate is the slope of the line.

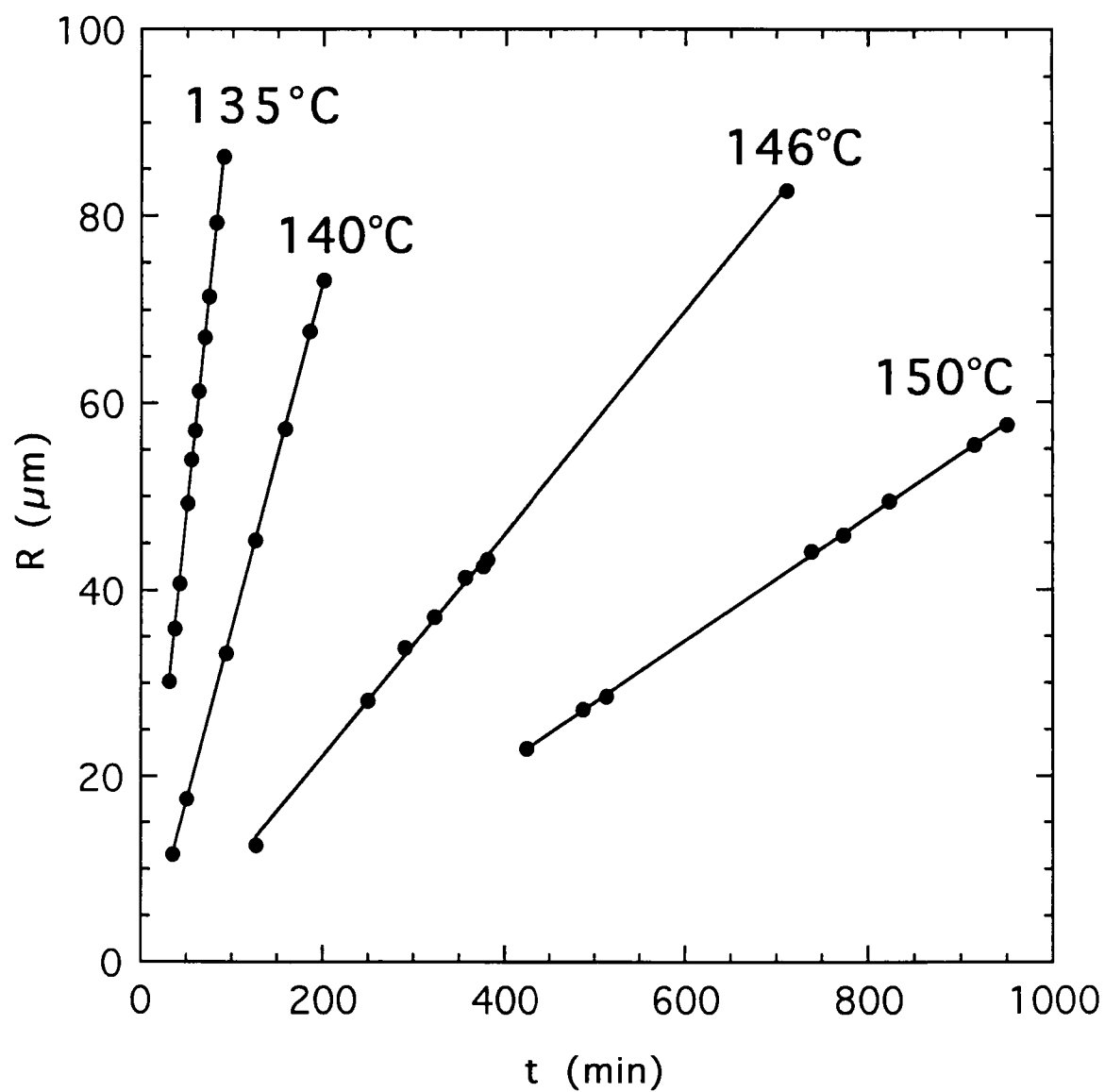


Fig.4.14 Spherulitic growth of iPPD for selected temperatures (135, 140, 146, and 150°C).

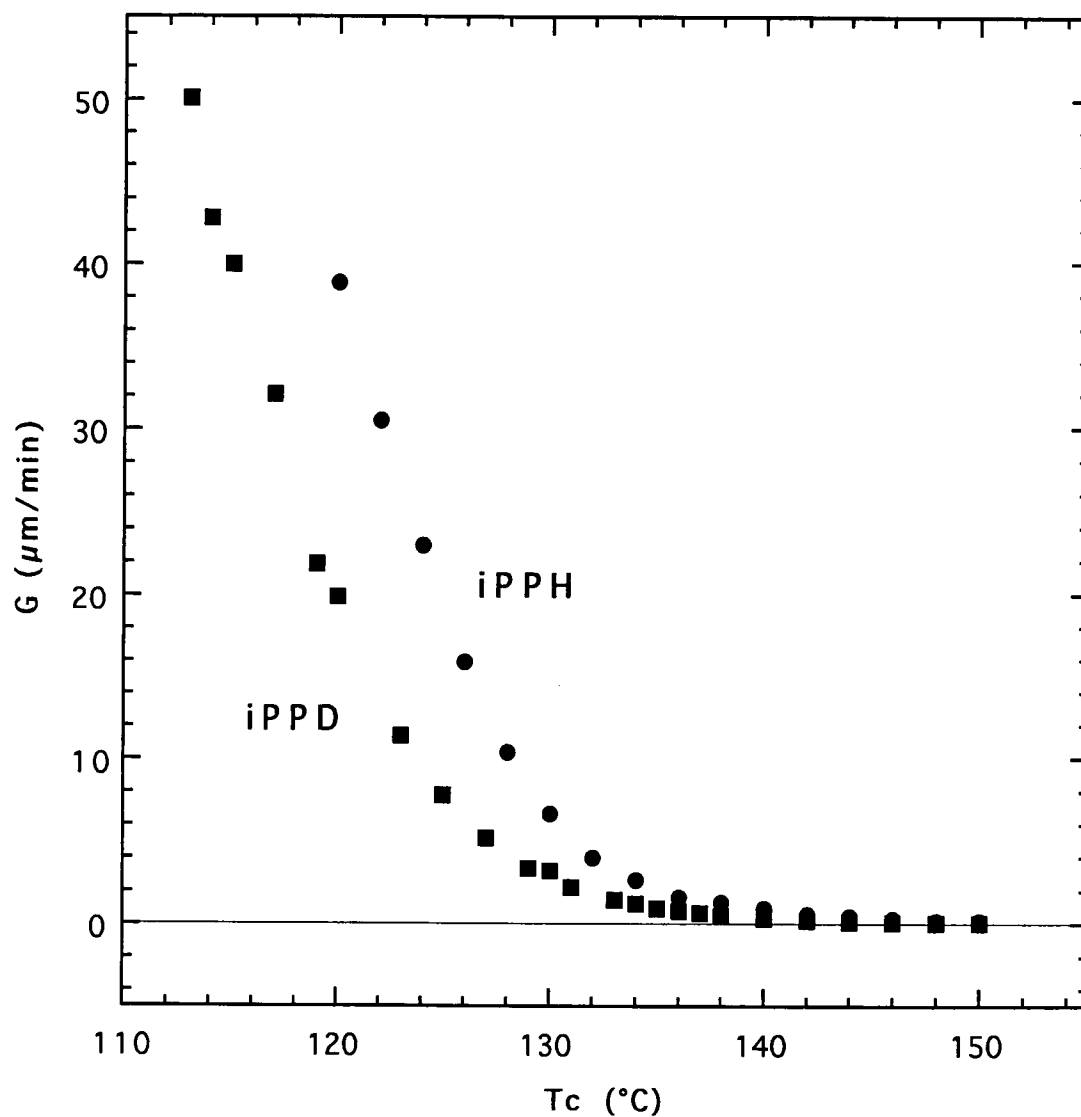


Fig.4.15 Growth rate, G , versus isothermal crystallization temperature, T_c , for both iPPD and iPPH.

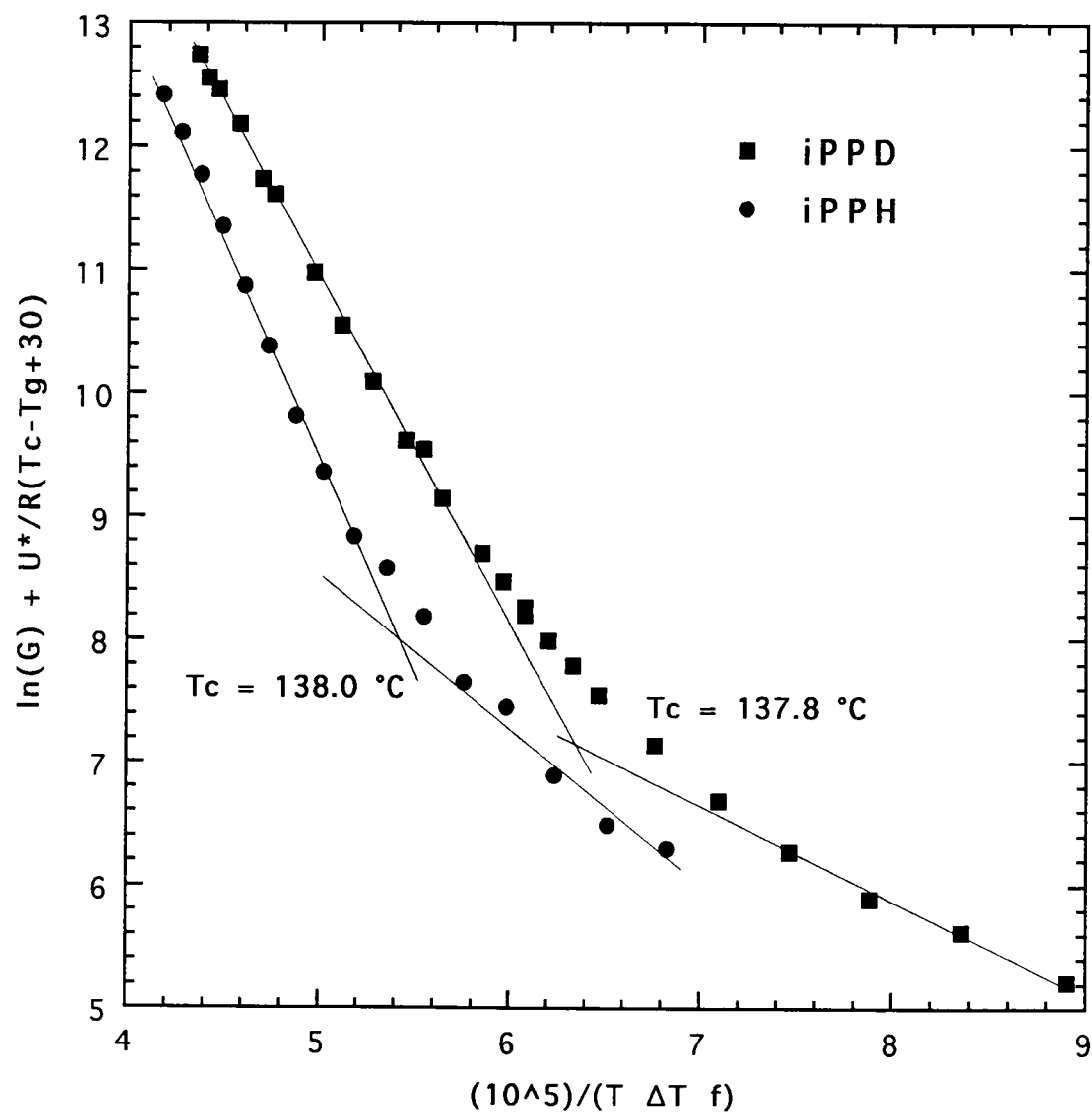


Fig.4.16 Secondary nucleation analyses using T_m^0 of 186.1°C and 177.4°C for iPPH and iPPD, respectively.

The effects of different values of the thermodynamic variables on the analyses and on the regime transition temperature of iPPD have been explored. Variation in T_m^0 has the greatest effect on the shape of the secondary nucleation plot, but does not significantly alter the regime transition temperature (T_m^0 values from 160°C to 210°C have been used). Use of the values of T_m^0 and T_g of iPPH for iPPD does not alter the transition temperature, but does modify the slopes, (Fig.4.17 and Table 4.3). Varying the values of U^* and T_g simply causes the curve to move up or down without changing its shape.

Although the transition breaks appear at different locations on Fig.4.16, because of the different values of T_m^0 , the actual transition temperatures are very close, 138.0°C for iPPH and 137.8°C for iPPD, (Table 4.4). It is therefore possible to conclude that the Regime II-III transition does not occur at a constant supercooling, but at a constant temperature in polypropylene. If this conclusion is generally applicable then it sheds considerable light on the nature of the Regime II- Regime III transition. The dependence on the thermodynamic temperature suggests that the location of the transition is controlled by some parameter with a simple temperature dependence and not the supercooling dependence that is characteristic of the Regime I- Regime II transition.

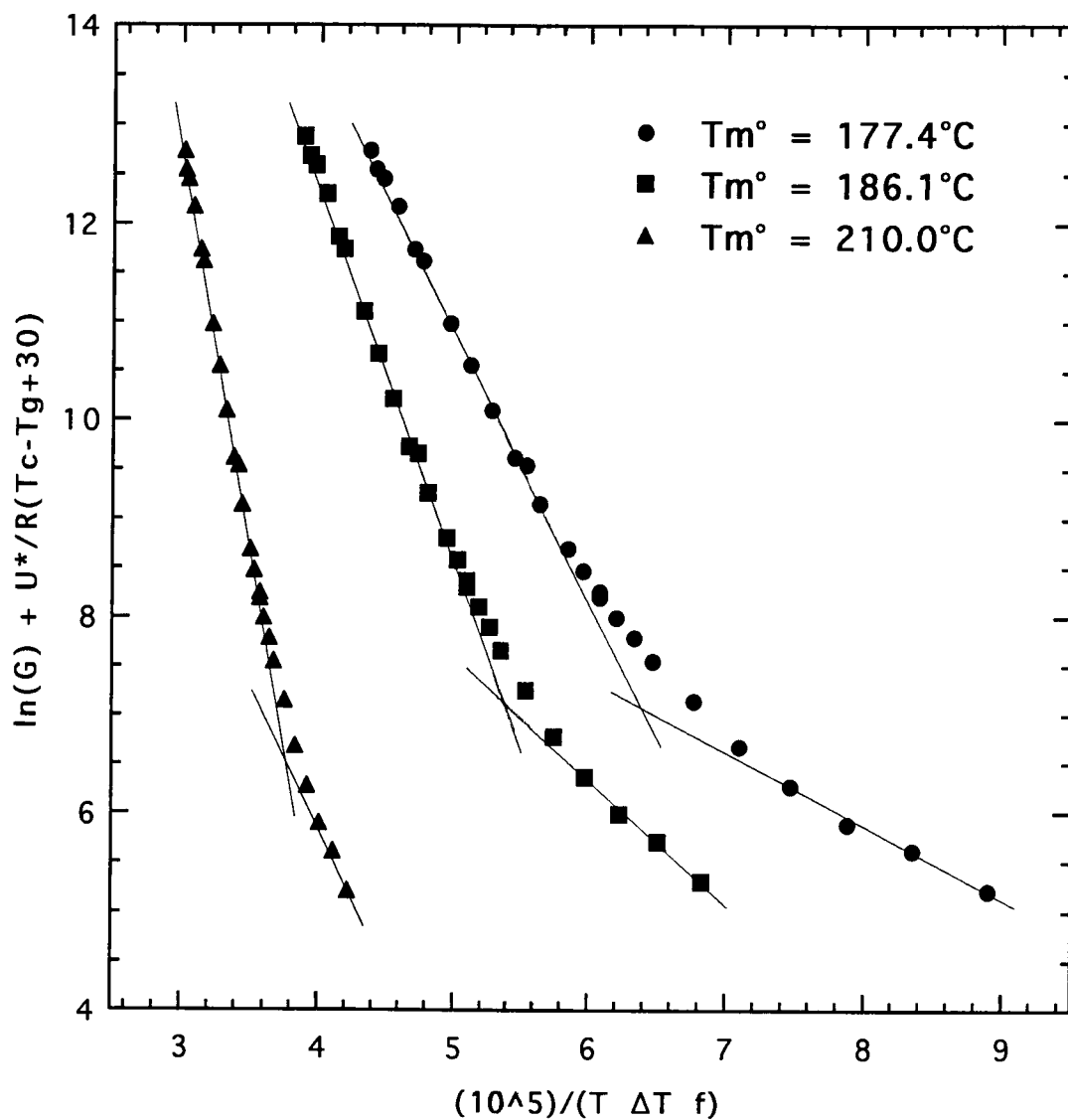


Fig.4.17 Kinetics analysis of iPPD with different values of T_m^0 .

Table 4.3: Surface free energy of iPPD for different T_m^0

T_m^0 (°C)	T_g (°C)	Regime	Regime Transition	K_g (10^5)	$\frac{K_{gIII}}{K_{gII}}$	$\sigma\sigma_e$ $\frac{\text{ergs}^2}{\text{cm}^4}$	σ_e $\frac{\text{ergs}}{\text{cm}^2}$
177.4	-16.5	II	137.8	0.717	3.8	276	30.0
		III		2.751		530	57.5
186.1	-12.0	II	138.2	1.330	2.8	503	54.6
		III		3.785		715	77.5
200.0	-16.5	II	138.7	3.701	2.2	1329	144.3
		III		8.054		1447	157.1

Notes: 1) σ is calculated from equation 2.5 to be 9.2 ergs/cm^2

2) $a_o = 5.486 \text{ \AA}$; $b_o = 6.256 \text{ \AA}$ {using the assumption that $(a_o b_o)_H / (a_o b_o)_D = 1.0014$ }

3) $\Delta H_f = 168.0 \text{ J/g}$; $\rho = 0.936 \text{ g/cm}^3$

Table 4.4: Surface free energy of iPPH and iPPD

Polymer	T_m° ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	ΔH_f (J/g)	Regime	Regime Transition	K_g (10^5)	$\frac{K_{gIII}}{K_{gII}}$	$\frac{\sigma\sigma_e}{\text{ergs}^2/\text{cm}^4}$	σ $\frac{\text{ergs}}{\text{cm}^2}$	σ_e $\frac{\text{ergs}}{\text{cm}^2}$
iPPH	186.1	-12.0	209	II III	138.0	1.365 3.659	2.7	641 860	11.5 11.5	55.9 75.0
iPPD	177.4	-16.5	168	II III	137.8	0.717 2.751	3.8	276 530	9.2 9.2	30.0 57.5

Notes: 1) Calculation was done on the assumption that the growth plane is the [110], $a_o = 5.49 \text{ \AA}$; $b_o = 6.26 \text{ \AA}$ for iPPH [13,21] and $a_o = 5.486 \text{ \AA}$; $b_o = 6.256 \text{ \AA}$ for iPPD.

2) $\rho = 0.936 \text{ g/cm}^3$ for iPPH and iPPD

3) σ is calculated from equation 2.5

The Regime II-III transition is envisioned as the point at which the rate of surface spreading becomes less than the rate of secondary nucleation. Surface spreading, for an adjacent reentry system, is essentially a reeling-in process dependent on the reptational ability of the polymer chain. One possible explanation could be that below the Regime II-III transition temperature the reeling-in rate is simply too low for surface spreading to occur, compared to the rate at which adsorbed stems can rearrange into simple stem nuclei. If this were true then it would be expected that the behavior would be influenced by the extent of entanglements in the melt, or by the critical molecular weight for entanglements. Both of these polymers are high molecular weight and close in actual values. So they would be expected to behave in a similar manner with regard to the reeling-in rate. If this explanation is correct then it would be useful to test it using polymers having molecular weights below the entanglement limit.

The slopes of the secondary nucleation plots can be used to estimate the fold surface free energies of the two polymers. In order for these calculations to be carried it is necessary to have estimates of the parameters which appear within equation 2.4. The equilibrium melting points have already been determined in this study and, to a first approximation, it is reasonable to assume that

$(a_0b_0)_H/(a_0b_0)_D = 1.0014$ (the volume ratio from Bates et al. [17]) since the deuteration has no effect on the c parameter. Clark and Hoffman [25] calculated the parameters of iPPH in the growth plane [110] to be $a_0=5.49\text{\AA}$ and $b_0=6.26\text{\AA}$, then using the previous assumption the parameters of iPPD are $a_0=5.486\text{\AA}$ and $b_0=6.256\text{\AA}$. The major unknown parameter is the latent heat of fusion. Its determination using conventional diluent or other extrapolation methods is laborious. As a first approximation we have assumed that an estimate of crystallinity combined with a DSC determination of heat of fusion can be used to determine the latent heat of fusion. Since DSC traces contain the effects of annealing and of melting followed by recrystallization during the heating scan on the measured heat of fusion, the technique has been applied to both iPPD and iPPH. The estimates obtained in this manner were 174.5 J/g for iPPH and 140.5 J/g for iPPD, the specimens used having crystallinities of 49.3% (iPPH) and 48.0% (iPPD). The accepted value for the latent heat of fusion of iPPH is 209 J/g [1]. If it is assumed that both polymers have similar systematic errors incorporated into the DSC determinations, because of their behavior during the heating scan, then a simple scaling of 209C using the values determined leads to an estimate of the latent heat of fusion of iPPD of 168 J/g.

When the calculations of $\sigma\sigma_e$ are made values (Table 4.4) are as follows: (1) for iPPH, regime II and regime III give $\sigma\sigma_e = 641$ & $860 \text{ erg}^2/\text{cm}^4$ respectively and (2) for iPPD regime II and regime III give $\sigma\sigma_e = 276$ and $530 \text{ erg}^2/\text{cm}^4$ respectively. In order to proceed further it is necessary to estimate σ independently. For this purpose the Hoffman modification of the Thomas-Stavely relation [119] is used (Equ.2.5).

Values of σ have been calculated as $11.5 \text{ erg}/\text{cm}^2$ for iPPH and $9.2 \text{ erg}/\text{cm}^2$ for iPPD. Substitution of these values into the determined values of $\sigma\sigma_e$ result in values of σ_e (1) for iPPH regime II and regime III of 55.9 and $75.0 \text{ erg}/\text{cm}^2$ respectively and (2) for iPPD regime II and regime III of 30.0 and $57.5 \text{ erg}/\text{cm}^2$ respectively. Surface free energies were also calculated for the wide range of T_m^0 s referred to earlier and are presented in Table 4.3 for completeness.

Regardless of the exact accuracy of these estimations, the most striking observation is the consistent reduction in the values of surface free energies that results in these cases. These reductions come in the case of the lateral surface free energy from the latent heat reduction and in the case of the fold surface free energy from a combination of the latent heat of fusion value and the changed slope of the secondary nucleation curve. So regardless of the accuracy of the latent heat determination, it is clear that the fold

surface free energy of iPPD is lower than that of iPPH. The most obvious origination of this effect is the known change in the bond length of C-D compared to C-H discussed previously by Bates et al. [17]. It is not possible to go into how this apparently minor change in a bond length could give rise to such a major change in fold surface free energy without carrying out a computer simulation of fold structures, something which is beyond the capabilities of this author. However, it is reasonable to presume that the shorter bond length results in less crowding between adjacent folds and also a lowering of the rotational potentials within an isolated fold. It does not, however, seem to the author that a change of the magnitude observed would be reasonable. Differences in the values of a_0 and b_0 from iPPH to iPPD would not be of sufficient magnitude to result in the observed differences.

4.2.2 Bulk Crystallization

Bulk kinetic results can be analyzed using Avrami and half-time analyses. Fig.4.18 shows several chart recorded bulk crystallization traces as a function of temperatures. Avrami's analysis take the lower values of each plot; i.e. before impingement. The half-time is the point where half of the intensity is reached. Fig.4.19 presents Avrami's analysis for different crystallization temperatures. It is remarkable that all plots have similar slope, n , and different intercepts, k .

Fig.4.20 shows that all n values fall between 4 and 2 and most of them are around 3 which means that most of the crystal growth is spherulitic. The lower values of n may represent growth in a form between sphere and disc or of thick discs. This make sense because at low supercooling the growth starts as spherulites but as they grow they reach the thickness of the sample and continue to grow as thick discs.

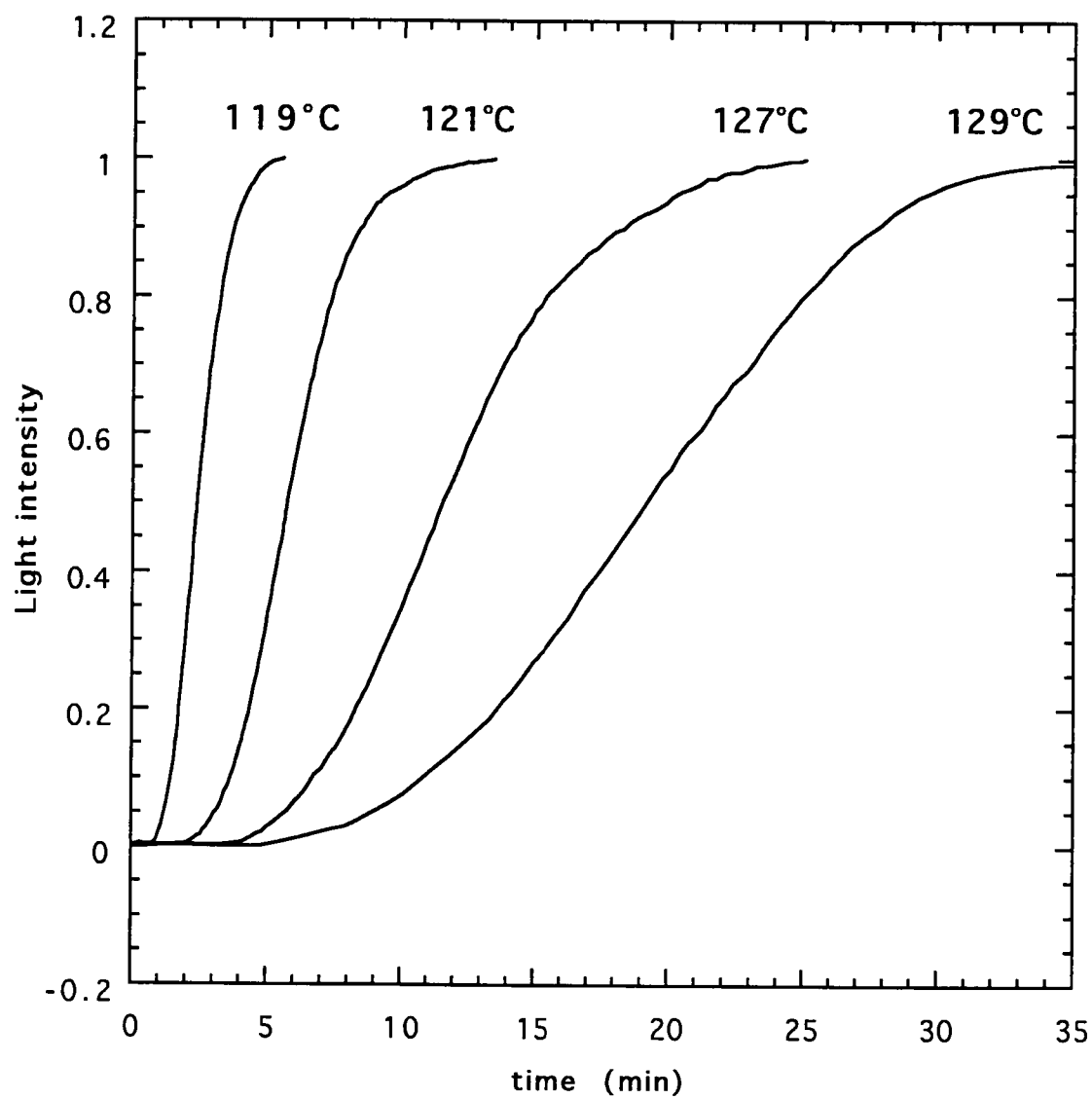


Fig.4.18 Isothermal bulk crystallization traces as a function of temperature (119, 121, 127, and 129°C) for iPPD.

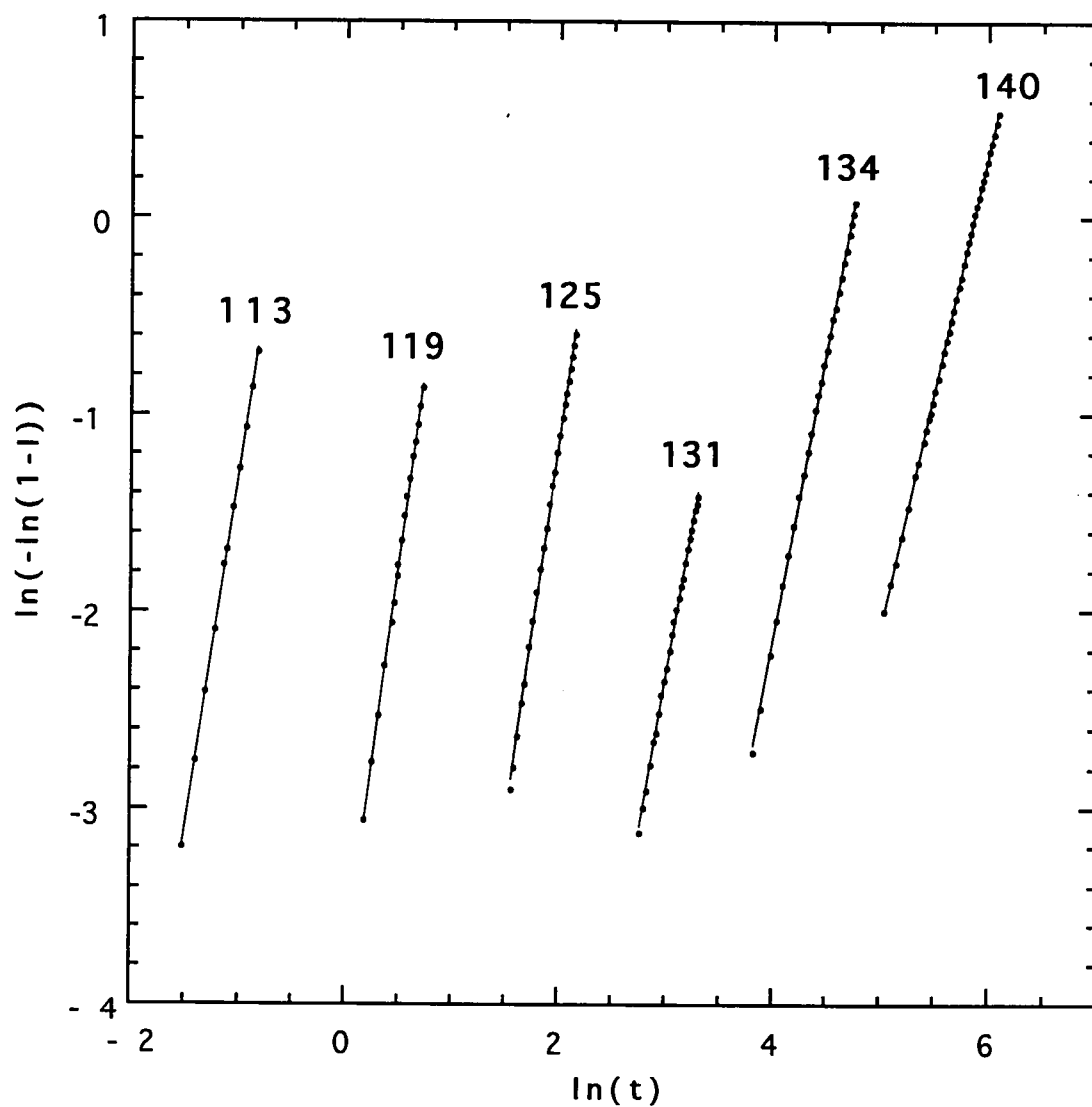


Fig.4.19 Avrami's analysis of iPPD for various isothermal crystallization temperatures (113, 119, 125, 131, 134, and 140°C).

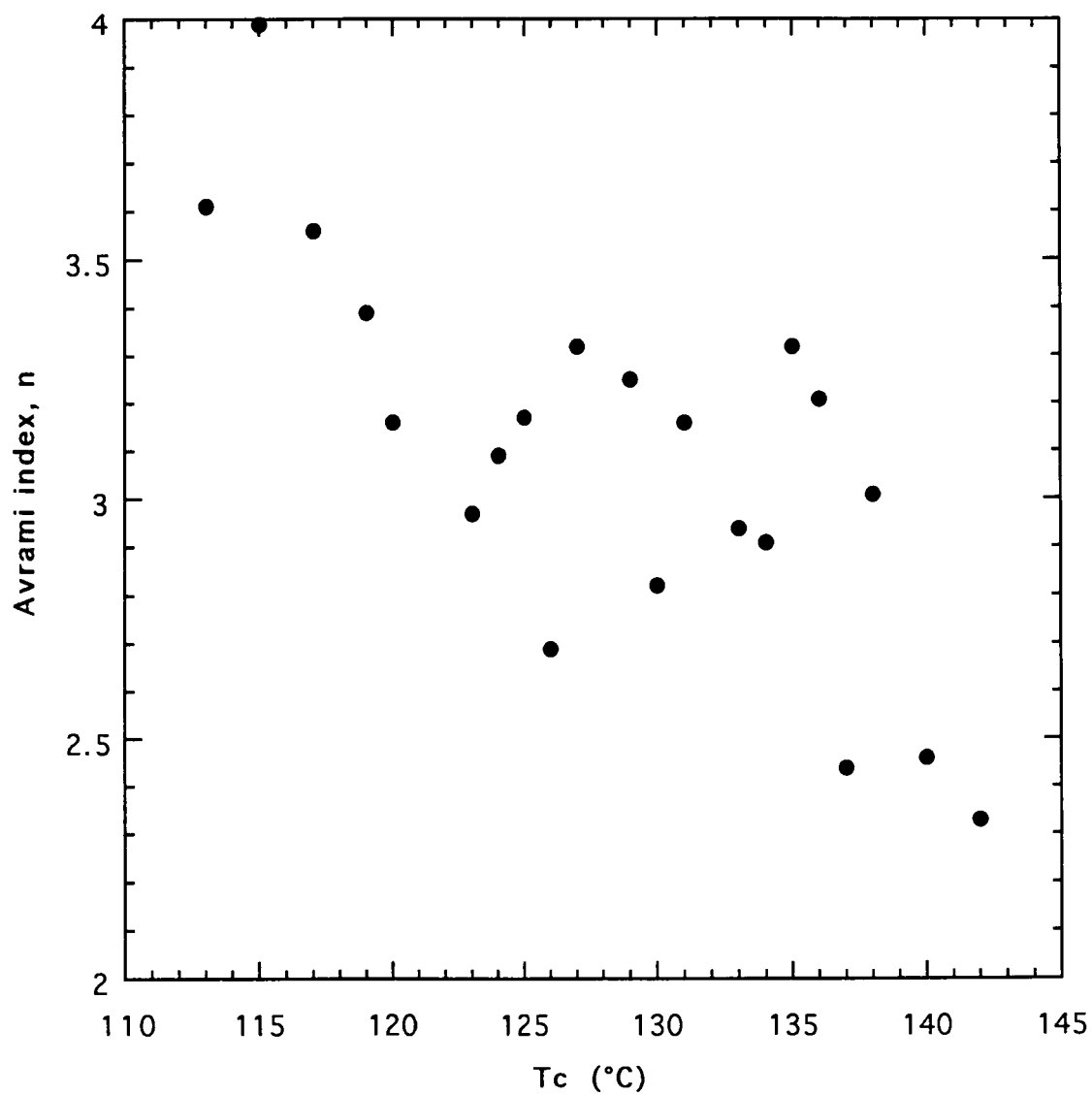


Fig.4.20 Avrami index, n , for iPPD as a function of isothermal crystallization temperatures.

Also the Avrami constant K was plotted as a function of crystallization temperature in a logarithmic plot, Fig.4.21. The shape of the curve is as expected since K is in direct relationship with the growth. At low supercoolings, starting from 136°C , K values become quite scattered and change direction. This is due either to the nucleation mode changing as explained before that spheres might change to discs or, perhaps, because of the regime transition that occurs close to 136°C .

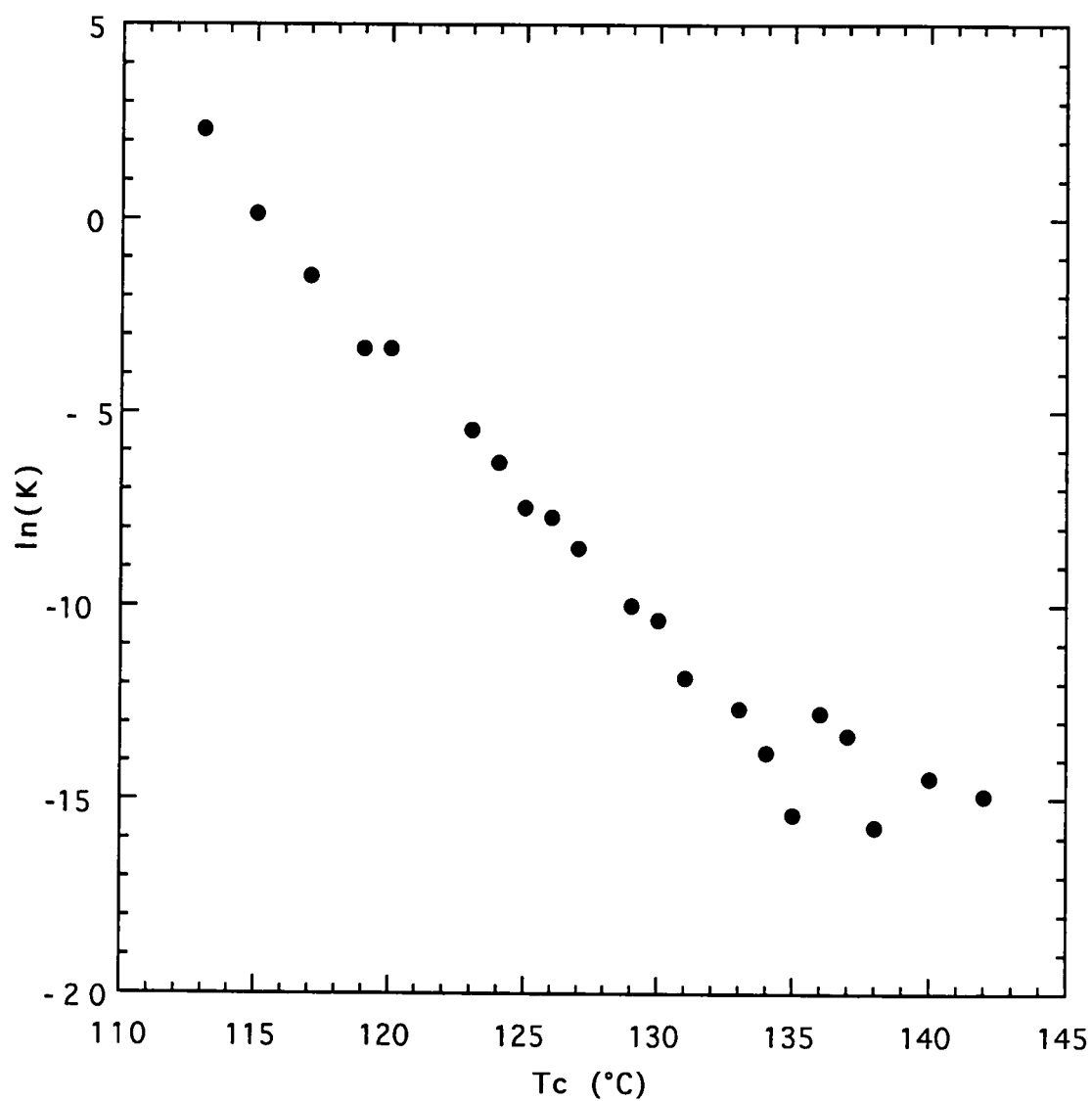


Fig.4.21 Avrami constant, K , for iPPD as a function of isothermal crystallization temperatures.

CHAPTER 5

CONCLUSIONS

5.1 Melting

The effect of lamellar thickening during polymer crystallization on equilibrium melting temperature, T_m^0 , has been investigated. For the same crystallization temperature iPP crystallized to impingement has a higher melting temperature than if crystallized for a lower crystallization time. Since T_m^0 is extrapolated from these melting temperatures, different values of T_m^0 are obtained depending on the time of crystallization. The results show that thickening in polypropylene favors the thicker lamellae and that it causes abnormally high extrapolated values of T_m^0 . Therefore, the 210°C estimate of the equilibrium melting point, even though accurately obtained, is erroneous. In addition, the equilibrium melting temperature that results from the data which is collected at low crystallization times is similar to the one obtained from DSC and SAXS experiments. Unlike polyethylene, the effect of thickening in iPP is greater at low supercooling.

The results show that for the same crystallization conditions, iPPD has a lower melting temperature than iPPH, and that the extrapolation of melting temperatures yields a lower equilibrium melting temperature than that to iPPH. The

difference obtained experimentally is close to that predicted theoretically of 8.7°C. Even though both polymers have different T_m^0 values, they both share the same slope of the extrapolated lines. As a consequence, for any crystallization temperature, T_c , the melting temperature of iPPD is lower than that of iPPH, in agreement with theoretical predictions.

5.2 Crystallization

Analyses of linear growth kinetics show that both polymers exhibit a Regime II - Regime III transition. The transition occurs at almost the same temperature for the two polymers, not at the same supercooling. It is hypothesized that this behavior results from the Regime II - Regime III transition being controlled by molecular mobility factors.

CHAPTER 6

RECOMMENDATION FOR FURTHER WORK

The idea behind studying the effect of deuteration on melting and crystallization is to find out whether iPPD will segregate from iPPH during crystallization. According to the results shown in this thesis, iPPD has lower crystal growth rate and lower melting temperature for any isothermal crystallization temperature. This indicates that segregation might be preferred at atmospheric pressure. However, there is no *a priori* reason to conclude that segregation will occur at elevated pressures. Consequently, studies of a mixture of iPPH and iPPD at elevated pressures is recommended with SANS.

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VITA

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