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Crystallization of Isotactic Poly(Propylenes) with Enhanced Melt Strength

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CRYSTALLIZATION OF ISOTACTIC
POLY(PROPYLENES) WITH ENHANCED MELT STRENGTH

By

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<tbody>
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<td>30%</td>
</tr>
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ABSTRACT

Copolymerization of propylene with 1,9 decadiene using an isospecific metallocene catalyst leads to isotactic poly(propylenes) with H-type intermolecular linkages, resembling chemical crosslinks and leading to enhanced melt strength. In this work we analyze the effect of very small concentrations of diene (0 – 400 ppm) added to the iPP chain on the crystallization, polymorphism and morphological behavior of two series of copolymers of this nature crystallized from their quiescent melts. These series differ in the intermolecular distribution of the incorporated diene. In reference to the homopolymer the H-linkages enhance the primary nucleation density and the overall crystallization rate increases substantially. This effect is particularly strong when the chains were exposed to diene from the start of the polymerization. A minimal variation in the linear growth rate between the linear and H-linked samples in both series indicated that the addition of ppm levels of diene does not change the chain microstructure significantly as to impact growth. Some structural changes caused by the H linkages led to higher contents of gamma polymorphs. The difference in distribution of the diene between the two series was confirmed by polymorphic analysis. Crystallinity was not affected by the addition of H-links.

The application of Avrami models to the overall crystallization data ruled out significant differences between nucleation mode and the crystal geometry of the linear and H-linked iPPs. Solid state $^{13}$C NMR indicated that the H-links in the amorphous regions slows short segmental relaxations of the diene containing samples in this region compared to the linear ones. The wide difference in nucleation rates is correlated with differences in melt dynamics, as the longest more branched molecules may retain some order prior to crystallization from their melt state. The addition of extra entanglements in the linear chain by diene incorporation affects the spherulitic morphology and lamellar stacking. Dynamic mechanical analysis suggested minimal variation in the mechanical properties between the linear and H-linked polypropylenes.
CHAPTER 1

INTRODUCTION

1 Synthesis, properties and types of polypropylene

Polypropylene (PP) was discovered in the early 1950s. Since then PP has grown into a commodity polymer with numerous grades for specific end uses. By controlling the polymer chemistry it is now feasible to generate rather versatile polypropylene materials. It serves double duty, both as a plastic and as a fiber. As a plastic it is used to make molded articles, packaging films etc. As a fiber, polypropylene is used to make indoor-outdoor carpeting; it works well for outdoor carpet because it is easy to make colored polypropylene, and because polypropylene doesn't absorb water. Structurally, polypropylene is a vinyl polymer, with the repeating unit: \(-[\text{CH}_2\text{-CH(CH}_3\text{)}]_n\)\-, made by the polymerization of high-purity propylene gas in the presence of an organometallic catalyst. Classical Ziegler Natta or more recent metallocene catalysts are used for polymerization. A Ziegler-Natta catalyst is a reagent or a mixture of reagents used in the production of polymers of 1-alkenes (\(\alpha\)-olefins). Ziegler-Natta catalysts are typically based on titanium compounds (usually halides) and organometallic aluminium compounds, for example, \(\text{TiCl}_4\) and ethylaluminium, \((\text{C}_2\text{H}_5)_2\text{ClAl}\). The mechanism of polypropylene synthesis using Ziegler Natta catalysts is shown in figure 1.2.

Polypropylene can be made with different tacticities. Propylene with structure \(\text{CH}_2=\text{CH}(\text{CH}_3)\) can have two distinct configurational arrangements of the repeat unit as shown in figure 1.1.

![Figure 1.1](image)

**Figure 1.1** Two different configurational arrangement of repeat units in polypropylene

1

In this figure 1.1 the dotted lines indicate bonds below and solid line indicates bonds above the plane of the paper. In spite of the substituted carbon atom being attached to four different groups (asymmetric), the stereoisomers do not show significant optical activity owing to the almost identical polymer chain residues attached to the asymmetric carbon atom. In isotactic polypropylene all repeat units have same configuration, whereas in syndiotactic the configuration alternates from one repeat unit to another. Atactic polypropylene has random placement of the two configurations. The tacticity of a polymer can have a dramatic effect on its physical properties. Atactic polypropylene is a soft, rubbery polymer, while isotactic polypropylene is strong and hard with excellent resistance to stress, cracking, and chemical reaction. The difference is attributed to the fact that isotactic polypropylene is crystalline due to its regular structure, whereas the atactic one is unable to crystallize owing to its irregular structure. The hardness and rigidity of the syndiotactic polypropylene is in between the two.

The Z-N catalysts polymerize α-olefins like ethene, propene (shown in fig 1.2), 1-butene etc. These catalysts are important for obtaining stereospecific polymers. The reaction takes place at the surface of the solid catalyst and the polymerization occurs through a π-complexation of monomer and transition metal followed by a four center anionic coordination insertion process in which monomer is inserted into a metal carbon bond as described in figure 1.2. The driving force for isotactic propagation results from steric and electrostatic interactions between the incoming monomer and transition metal ligands. The propagation chain terminates in most cases via chain transfer reactions.

During the polymerization process of propene, addition of monomer units at the chain end in head to tail manner and in the same stereo arrangement results in the formation of isotactic polypropylene (iPP). Any mistake made by either a change of insertion mode, i.e. head to head or tail to tail, or stereo irregularities is termed as defect. If a polypropylene unit is added to the chain in a head to head or tail to tail manner, a regio defect results. The presence of a polypropylene repeat unit with a configuration opposite to that of its immediate neighbors represents a stereo-defect in an otherwise identically recurring repeat unit structure\(^1\).
Figure 1.2 Z-N catalyzed polymerization of propylene
1.2 Melt strength of isotactic polypropylene

Isotactic polypropylene (iPP) is a useful thermoplastic with wide range of applications because of properties such as high tensile strength, hardness, and chemical resistance\(^3\). However, its predominantly linear structure combined with high entanglement molecular weight leads to low melt strength and suffers from poor processability in processes involving melt stretching. Entangled molecular weight, \(M_e\), defined as the molecular weight between adjacent temporary entanglement points, for IPP, \(M_e^4 = 6900\, \text{g/mol}\). The same problem is not encountered with polyethylene melts because their \(M_e\) is much lower, \(\sim 1200 \, \text{g/mol}\)\(^5\). Thus, it has been difficult to use polypropylene resins in certain processing methods dominated by extensional flow, for example blow molding, foaming, and thermoforming. The melt strength (MS) of a polymer is defined as the maximum force at which a molten thread can be drawn under standard conditions before it breaks. High values of MS are desired in film and other processes where the molten material is stretched prior solidification.

Strain-hardening is generally attributed to the presence of long chain branches owing to increased number of entanglements per branch. The relative melt strength can be tested by comparing the level of strain hardening\(^6\). The extent of strain hardening of polymer melts at a given strain rate can be obtained from the ratio of the extensional viscosity to the linear viscosity at the break point. Strain hardening is the acceleration of elongational viscosity growth with strain that takes place beyond some characteristic strain\(^7\). Increasing the average molecular mass of a polymer results in higher shear viscosity, as well as higher MS. However, MS increases much more rapidly upon the addition of long chain branches on the polymer backbone\(^8\) due to increase in entanglements (considering that molecular mass between branch points is much larger than the entanglement molecular mass). Many studies\(^15, 9, 10\), have shown that the long chain branched polymer fractions usually reside in the high MW end. In these reports it was evidenced that compared to homopolymer, all the LCB samples show a tail in the high MW end, the tail usually becomes a shoulder and the MWD becomes much broader at high LCB distributions. These small fractions of LCB polymers play a decisive role in improving rheological properties.

An increase in zero shear-rate viscosity is found for LCB polymers in the case where the molecular mass between branch points is much larger than the entanglement molecular mass (\(M_e\)). For a high branching density the molecular mass between branch points becomes small.
and therefore leads to a reduced zero shear-rate viscosity in comparison to linear polymer\textsuperscript{11}. The reduction of zero shear-rate viscosity due to high density of long-chain branching is attributed to the reduced radius of gyration. LCB also reduces polymer hydrodynamic volume, as a result the LCB polymers are more prone to be disentangled than the linear ones at high shear rates, and therefore they are expected to have better shear thinning properties.

1.3 Factors affecting flow induced crystallization of polymers

The molecular weight and its distribution not only affect the rheological properties, but also influences the flow induced crystallization behavior. In most polymer processing operations, such as extrusion, injection molding, fiber spinning, etc., the molten polymer is exposed to various levels of flow fields causing orientation and crystallization of polymer molecules from the melt, which strongly influences the final polymer properties. In isotactic polypropylene (iPP), the flow-induced morphology, characteristic features of the crystalline phase, and its crystal form, (\(\alpha\), \(\beta\) or \(\gamma\)) in the final product have a direct effect on the product properties and performance. Some key factors that influence the effect of flow on the orientation and structural evolution includes the polymer molecule architecture such as the chain rigidity, interchain friction, chain branching, chain length and its distribution.

In flow-induced crystallization\textsuperscript{12,13,14}, it is generally accepted that orientation of polymer molecules in the flow direction causes extension of chains, lowering the conformational entropy and thus reducing the free energy barrier for crystal formation. It has been speculated that these extended chains can undergo a phase transition and lead to formation of mesophase or transient state, which can act as nuclei to the crystallization of neighboring chains in the random coil state\textsuperscript{21}. The net result is an increase in the number of nuclei and crystallization rate. However, at a given shear rate, only the polymer molecules above a critical orientation molecular weight (\(M^*\)) in the distribution become oriented at a given shear rate. \(M^*\) is defined as the minimum molecular weight needed for the chain to become oriented and to form stable nuclei at a given shear rate. The \(M^*\) for iPP was calculated by Hsiao, et al.\textsuperscript{19} to be around 300,000 g/mol for the following conditions: temperature of 150°C, shear strain of 1428 % and shear rate of 57s\textsuperscript{-1}.

Studies related to the effects of molecular weight on flow induced crystallization of linear polymers concluded that with increase of either the \(M_w\) or the degree of polydispersity, the crystallization under a given flow increases. This is so because the high molecular weight chains
take longer time to relax than low molecular weight ones after application of shear, and therefore retain some orientation in the melt prior to crystallization. Specifically for iPP, many reports have documented the effect of increase in crystallization rate under shear with increase in Mw, for example, Monasse and coworkers\textsuperscript{15} performed fiber pullout experiments at 125–130°C using three iPP polymers that differ in M\textsubscript{W}. An exponential increase in crystallization rate with increase in M\textsubscript{w} was documented by these authors. Another rheological study of iPP polymers with differing M\textsubscript{W} and broad MWD at 138–140°C by Vleeshouwers and Meijer\textsuperscript{16} showed that the high molecular weight tail enhanced the crystallization after shear and long polymer molecules were predominantly responsible for the formation of highly oriented surface layers due to shear. Kornfield et al.\textsuperscript{13} blended a high molecular weight iPP (923kg/mol) with one having lower molecular weight (186kg/mol) and observed that the addition of less than 1\% of chains with M\textsubscript{w} five times larger than the M\textsubscript{w} of the base resin profoundly affects the crystallization kinetics and crystalline morphology from a sheared melt.

Several other reports have also documented the above observation for isotactic polypropylene\textsuperscript{17,18,19,20,21,22}. However, the effects of the long chain branching (LCB) in polymers on crystallization, especially in polypropylene have not been published to such an extent so far. For a given polymer molecular weight, the LCB is expected to hinder the relaxation behavior of molecules in the melt, and in turn affect the morphological features of the crystallized polymer. Only a few publications have reported that LCB also increases the rate of crystallization under shear for various polymers like PE (polyethylene)\textsuperscript{23, 24}, PP \textsuperscript{25,26,34} and PET (polyethylene terephthalate)\textsuperscript{27}.

Long polymer chains with longer relaxation times are more prone to forming oriented nuclei under flow as has been evidenced for iPP by adding UHMWPE as long chain additive\textsuperscript{26}. Under the experimental conditions (T\textsubscript{c} =145°C and shear rate 60s\textsuperscript{-1}), UHMWPE remained a noncrystalline moiety forming an oriented scaffold structure and thus inducing iPP nucleation. Relaxation times of the iPP chains at the iPP/UHMWPE interface become significantly retarded, this enables the retention of molecular orientation after shear and induces the formation of oriented nuclei, but the increase of the UHMWPE content promotes phase separation between iPP and UHMWPE, leading to a lesser nucleating effect\textsuperscript{26}.

Recently, Agarwal et al.\textsuperscript{37} synthesized LCB iPP made by copolymerizing propene with ppm levels of 1,9 decadiene. They observed that under shear the crystallization rate increased by
one order of magnitude for the LCB polypropylenes, and, attributed the difference to an increase
in crystal nuclei due to orientation of the polymer molecules and the formation of a stable
crystallization precursor structure in the sheared melt. The $M_n$ was not much affected by the
diene incorporation, however, the weight-average $M_w$ increased dramatically with the increase
of 1,9-decadiene concentration thus changing the MWD. This increase in $M_w$ could also be a
probable reason for the observed increase in nucleation under shear.

In summary, any factor that increases the relaxation time of molten polymer chains
during crystallization under shear, such as increase of $M_w$ or formation of LCB, will help to
retain some orientation in the melt prior to crystallization, and thus enhance the formation of
oriented nuclei enabling faster rate of crystallization.

### 1.4 Advantages of metallocene catalyst compared to conventional Z-N catalyst for synthesis
of well defined LCB polyolefins

Most of the approaches for formulating LCBiPP employed post reactor technologies such
as irradiation$^{28,29}$, peroxide decomposition$^{30,4}$, and grafting$^{31}$. Generally, the irradiated or
peroxide-treated products are complex in branching structure, and consistency of the process
may be difficult to control. Grafting techniques also offer another means to produce branched
polymers, but the preparations of polyolefin graft copolymers are usually not straightforward.

Polymers produced by Ziegler Natta catalyst possess broader distribution of chains than
one would expect from a single active center, and the resulting polymers generally have a
broader distribution of properties. Limited knowledge about the catalyst structure, and not being
able to modify or design specific structures, makes it difficult to understand what features in the
catalyst result in specific polymer properties. In contrast, metallocenes have well defined
chemical structures that can be isolated. These structures have a single active polymerization site
with uniform ligand environment that makes the resulting polymer chains with uniform
architecture and narrow distribution of properties. Knowledge of the metallocene catalyst
structure allows study of the relationship between its geometry and the product architecture, and
by modifying the catalyst structure, it is possible to tailor the iPP product properties to meet
market requirements$^{32,33,39}$.

Thus, the advent of metallocene technology has significantly impacted the polyolefin
industry. Metallocene catalysts not only enable the production of polyolefins with narrow
molecular-weight distribution (MWD), narrow chemical-composition distribution (CCD), and precisely controlled polymer stereoregularity, but they also allow the introduction of long-chain branch (LCB) during the olefin polymerization by incorporating in situ generated or externally added vinyl terminated macromonomers or by crosslinking with 1,3-benzenedisulfonyl azide. The single step method of producing LCB-PP during olefin polymerization by metallocene catalyst (which is of more technological interest because of its inherent simplicity) is carried out by copolymerization with non-conjugated dienes. Introduction of LCB in iPP prepared by Ziegler Natta catalysts, required two steps.

1.5 Effect of molecular weight on quiescent crystallization rate of polymers

The main factors that govern and control the iPP growth rates are concentration of defects (including branching) and molar mass. An increase in any of these parameters leads to a decrease in linear growth rate.

A small but systematic decrease of growth rate with molar mass was observed for metallocene and Z-N catalyzed isotactic PP fractions, poly aryl ether ketone, PE, PLLA and cis 1, 4 polybutadiene. The results from a review by Okui and Umemoto suggested that the molecular weight dependence of maximum growth rate can be scaled and expressed as a -0.5 power of molecular weight to all crystalline polymers, i.e. \( G \alpha M^{-0.5} \) at a given undercooling. The variation of rate with molar mass is attributed to the increased number of entanglements per chain in the melt, which affects segmental transport in the crystallization process. Increasing concentration of comonomer that lies outside the crystalline region (defects) also substantially reduces the growth rate.

Analysis of the effect of molecular weight on overall crystallization from sheared and quiescent melts of PP, PE and other polymer systems have been studied by various research groups but the conclusions of the influence of molecular weight on the crystallization kinetics is not uniform among these works, and there are certain ambiguities. For example considering overall crystallization rates of iPP, Alamo et al studied isothermal crystallization in a set of Z-N fractions where the Mw ranged from 97-328K g/mol, and, Carvalho et al analyzed the non isothermal crystallization kinetics of iPP samples with range of Mw between 84-1400K g/mol. Both of them have demonstrated that quiescent overall crystallization rate increases with increase in molecular weight whereas De Rosa (range of Mw, 85-629K g/mol) observed an opposite
effect for metallocene catalyzed iPP. Galante et al.\textsuperscript{51} (Mw range, 68-288K g/mol) observed that molecular weight had no significant effects on the crystallization kinetics of metallocene catalyzed iPP. Recently Elmoumni et al.\textsuperscript{20} observed that for quiescent crystallization, addition of a small fraction of high molecular weight iPP (Mw = 302kg/mol) to low molecular weight one (Mw = 140kg/mol) increases the nucleation density by a factor of almost 5, as estimated from optical microscopy. For metallocene catalyzed linear PE’s, Wilkes, et al.\textsuperscript{52} and Fu, et al.\textsuperscript{53} observed that an increase in Mw decreased the crystallization rate. Similarly for poly butylene adipate\textsuperscript{54} a decrease in crystallization rate was observed with increase in molecular weight.

1.6 Effect of LCB on quiescent crystallization rate of polymers

The effect of LCB on spherulitic growth rates has not been studied extensively for isotactic PP’s, only Yan, et. al.\textsuperscript{55} observed that spherulites of LCBPP grow slower than its linear counterpart. Recently a paper\textsuperscript{56} comparing the effect of molecular weight and branching on the growth rate behavior of PLLA (poly L-lactic acid) has been published. In this report the physical properties, crystallization, and spherulite growth behavior of linear and 3-arm poly (L-lactide) [i.e., poly(L-lactic acid) (PLLA)] have been investigated. The findings in the paper supported that branching disturbs thickening (or growth) of the crystallites at a constant $T_c$ from the melt and increases the lattice disorder of the formed crystallites. It was also demonstrated that at a fixed molecular weight the growth rate (G) of branched PLLA was much lower than linear PLLA. The exclusion of branch points from the crystalline region was cited as the probable reason for the observed decrease in growth rate. Analysis of the effect of molecular weight on the growth rates led to the conclusion that there was a monotonic increase of the growth rate of linear PLLA with decreasing molecular weight. The H-linked iPP’s in the present study can be treated as a 4 arm star molecule since the length of the comonomer, 1,9decadiene is much smaller than the length of iPP chains. Therefore, comparing the results of overall crystallization and spherulite growth rate of these H-linked iPP’s with their linear counterpart may provide some insights regarding the effect of the links on the nucleation behaviour influencing the overall rate and also the irregularities conferred to the linear chain dictating the growth rate.

The LCB introduced in iPP by peroxide grafting or electron beam irradiation seems to increase the rate of overall non isothermal crystallization from quiescent melt\textsuperscript{57,58,59}. It has been observed by various research groups that grafted PP appears to act as a nucleating agent for the
matrix and accelerates the crystallization rate\textsuperscript{60, 61}. Guldogan et al.\textsuperscript{62} and Seo et al.\textsuperscript{63} speculated that the different crystallization behavior between PP-g-MA and PP is due to a chain interaction, such as hydrogen bonding between hydrolyzed maleic anhydride groups. The free energy of formation of a critical nucleus on the growing crystal surface remains almost the same for both of them, but the hydrogen bonding in g-PP decreases its diffusional activation energy compared to that of ungrafted one. Therefore, the effective nuclei for MA-g-PP increases by almost ten times as compared to iPP, resulting in a subsequent increase in the crystallization rate of grafted PP.

It has also been speculated that the decrease in molecular weight induced by the grafting\textsuperscript{64} or electron beam\textsuperscript{58} reduces the entanglements of PP molecules and consequently increases their ability to order, and, enhances overall crystallinity. In addition to LCB formation, grafting or electron beam radiation on iPP leads to a decrease in average molecular weight in most cases. Therefore, the increase in crystallization rate of these grafted or irradiated samples could be a consequence of either the reduction in molecular weight or formation of LCB. However, to emphasize the influence of LCB solely on the crystallization rate, few reports evidenced that the increase of crystallization rate from quiescent melts is indeed a consequence of addition of LCB, as the molecular weight remained almost similar compared to the original linear PP\textsuperscript{65,66}. The model LCB iPP’s chosen for the present study can highlight and clarify the individual influence of both the LCB and molecular weight on the crystallization rate from quiescent melts.

Studies concerning the effect of LCB on the crystallization kinetics of olefin copolymers have been published as well. Alamo et al.\textsuperscript{67} observed that at a given Tc the LCB containing ethylene-octene copolymer crystallizes at an appreciably slower rate compared to the same copolymer devoid of any LCB. The decrease in crystallization rate for the branched ethylene copolymers compared to linear PE is expected since the branches disrupt the regularity of sequences in polymer chain and thereby hinders the ordering of molecules in the chain\textsuperscript{68,69,53}. On the contrary some of the reports\textsuperscript{70,71} evidenced the enhancement in quiescent isothermal crystallization rate of LCB PE, the LCB was introduced in linear PE by melt blending with another LCB containing PE.

The effect of chain branches on crystallization kinetics has been studied for a few other polymeric systems. For PET\textsuperscript{72} and polycaprolactones\textsuperscript{73} it was observed that relative to the linear
sample, nucleation and growth were retarded for all branched samples except for the one with fewer branches.

From the above examples of previous literature cited it can be stated that the difference in molar mass or branching influences the nucleation activity which is directly related to the overall crystallization kinetics of polymeric systems. The linear growth rates are not affected by nucleation density, therefore, they are a better measure of the effect of defects and irregularities conferred to the iPP chain by the LCB junctions on the crystallization rates. A measure of the growth rate of the spherulites during crystallization until the time of impingement provides a wealth of information regarding the mechanism of crystallization in the polymer, and has been the focus of several investigations\textsuperscript{74,75}.

A compendium of literature work on studies of the effect LCB polymer in reference to linear one on the crystallization rates from sheared and quiescent melt is provided in the tables below.

The tables include the journal citation, types of sample, condition of the melt from which crystallization takes place, i.e, shear or quiescent and a brief summary of the results obtained. The effect of LCB on the crystallization rate of linear chains of polypropylene (table 1.1), polyethylene (table 1.2) and other polymers (1.3) are separately summarized in these tables.

<table>
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<td>Journal of Applied</td>
<td>Virgin PP, reactive</td>
<td>Quiescent,</td>
<td>LCB PP crystallizes faster than linear, the rate increases with increasing</td>
</tr>
<tr>
<td>polymer science</td>
<td>extrusion with peroxide, to produce LCB.</td>
<td>non-isothermal</td>
<td>amount of peroxide.</td>
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<td>(1996, 61, 1395)</td>
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<td>Wang, et al.</td>
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<td>Macromolecules</td>
<td>LCBiPP-Metallocene</td>
<td>Shear, and quiescent</td>
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</tr>
<tr>
<td>(2003, 36, 5226)</td>
<td>catalyzed.</td>
<td>non isothermal</td>
<td></td>
</tr>
<tr>
<td>B.Hsiao, et al.</td>
<td>In situ diene incorporated</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.1 - Continued

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colloid Polymer science (2004, 282, 381) Stranz et al.</td>
<td>Mechanically milled iPP</td>
<td>Quiescent, non-isothermal</td>
<td>With increase in cryogenic milling LCB formation occurs which increases Tc consistently</td>
</tr>
<tr>
<td>Colloid Polymer science (2005, 284, 322) Zeng et al.</td>
<td>LCBiPP, MFI=2.1 Mw=396000 Linear, MFI=7.0</td>
<td>Quiescent</td>
<td>Spherulitic growth rate of LCBiPP is lower than linear.</td>
</tr>
<tr>
<td>Journal of applied polym science (2006, 100, 2770) Voigt et al.</td>
<td>Electron beam irradiated LCBiPP, MFI=0.3 Polydispersity=4.2</td>
<td>Quiescent, non-isothermal</td>
<td>The Tc increases with LCB because of increase in nucleation density with LCB.</td>
</tr>
<tr>
<td>Journal of macromolecular sc.-B(2006, 45, 969) Tian, Zhou</td>
<td>PP, LCB introduced by peroxide grafting</td>
<td>Quiescent, isothermal and non-isothermal</td>
<td>The rate of both isothermal and non-isothermal crystallization increases with amount of LCB.</td>
</tr>
</tbody>
</table>

Table 1.2 Literature survey on crystallization of LCB PE

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Journal of polymer science-partB (1996, 34, 2317) Shroff et al.</td>
<td>Commercial grade HDPE-High polydispersity, LCB introduced by pelletization of resin</td>
<td>Quiescent and shear</td>
<td>The small amount of LCB enhances isothermal crystallization rates. The effect is similar for both shear and quiescent melt</td>
</tr>
<tr>
<td>Journal of thermal analysis (1998, 52, 275) Wagner et al.</td>
<td>Metallocene catalyzed HDPE melt blended with LCB PE (octane content as high as 9.5%)</td>
<td>Quiescent (non-isothermal). Different weight fractions of LCB PE blended with HDPE</td>
<td>There was an increase in crystallization rates, proportionally with the addition of LCB PE.</td>
</tr>
</tbody>
</table>
### Table 1.2 - Continued

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Journal of applied polymer science (1999, 74, 3153) Yamaguchi et al.</td>
<td>LLDPE + LDPE, Metallocene catalyst</td>
<td>Quiescent, non-isothermal</td>
<td>With higher weight % of LDPE in the blend the Tc of LLDPE increases suggesting an increase in the non-isothermal crystallization kinetics. LDPE was found to be a nucleating agent for crystallization of LLDPE</td>
</tr>
<tr>
<td>Polymer (2000, 41, 8813) Alamo et al.</td>
<td>Ethylene octene copolymers</td>
<td>Quiescent, isothermal</td>
<td>LCB containing copolymer crystallizes at appreciably slower rate.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 1.3 Literature survey on crystallization of LCB containing polymers (other than PE or PP)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample</th>
<th>Condition</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Journal of applied polymer science (1999, 74, 59) Jayakannan et al.</td>
<td>PET, linear and branched</td>
<td>Quiescent, non-isothermal</td>
<td>The presence of branches, kinks and linear disruptions in small concentration appear to enhance the crystallization compared to linear by facilitating nucleation, but at higher concentration of branches the crystallization process slows down.</td>
</tr>
<tr>
<td>Macromolecules (2004, 37, 3745) Kwak et al.</td>
<td>Polycaprolactones, comparison of hyperbranched and linear of comparable molecular weight</td>
<td>Quiescent, non-isothermal</td>
<td>During non-isothermal crystallization, the HPCL with fewer branches experience faster rates than linear one whereas HPCL with higher branches have slower rate.</td>
</tr>
<tr>
<td>Biomacromolecules (2005, 6, 240) Tsuji et al.</td>
<td>PLLA, Linear and 3 arm star having comparable molecular weight</td>
<td>Quiescent, non-isothermal</td>
<td>The 3 arm star PLLA has higher Tc than linear suggesting increase in crystallization rates with branching.</td>
</tr>
</tbody>
</table>
1.7 Other crystalline features affected by molecular weight and branching

Experimental data for spherulitic growth rates are generally analyzed using nucleation theory. The crystallization process is controlled by primary nucleation and growth. Primary nucleation is the formation from the melt phase to a new three-dimensional solid phase. Primary nuclei build up sporadically at random sites in the melt when the polymer melt is cooled down below its equilibrium melting temperature. Growth is a step in which the crystal nuclei grow through the addition of polymer chains onto the nuclei surface. Application of nucleation theory to the linear growth rate data of iPP often exhibits a distinct and rather abrupt upward trend in the spherulite growth rate vs. temperature curve as the crystallization temperature is lowered. This departure from conventional nucleation theory has been associated with the regime transition. Generally, the aforementioned data are much better fitted on such plots by two straight lines than one, suggesting the presence of a transition, called “regime” transition. This occurs when the rate of crystal growth differs from surface nucleation rate. This transition is strongly dependent on the undercooling (defect content) and molecular weight. As a result, the effect of molecular weight and defects induced by H-linkages on the regime transition of isotactic polypropylene can be understood by analyzing the linear growth rates according to temperature coefficient.

The degree of crystallinity is a very important parameter for the finished polymeric products and probably it has the same significance as the rate of crystallization does during processing of polymers. The final crystallinity determines the rigidity and transparency of the product. Degree of crystallinity plays an important role in determining the morphological, physical and mechanical properties of the polymer. It has been observed from earlier studies that the overall crystallinity decreases with increase in defect content and molecular weight. The mutual chain entanglement restrains the mobility of the macromolecules to a great extent causing hindrances to crystallization. The effect of chain entanglement is much more pronounced in case of high molecular weight polymers as they have longer chains.

1.8 Polymorphism in iPP and factors affecting the morphology

Isotactic polypropylene (iPP) is on one hand an ‘ordinary' commodity polymer with a very simple chemical structure. On the other hand despite its chemical simplicity it shows a remarkable complexity of crystal structures, and self-assembly behavior. Control of the growth of different polymorphs as a function of material grade and crystallization conditions is of great
technological importance. Isotactic polypropylene (iPP) presents complex polymorphic behavior. At the unit cell level, isotactic polypropylene exhibits three major polymorphic forms (α, β, and γ forms)\(^ {79}\) and a mesomorphic form\(^ {80}\). The appearances of the different polymorphic forms of isotactic poly(propylene) are critically dependent upon the crystallization conditions. All the polymorphic forms are characterized by chains in the stable 3-fold helical conformation. Temperature, pressure, catalyst, defects and external nucleants (for β form) are the major variables influencing the content of the different polymorphic forms.

In recent papers it has been clearly shown that the formation of gamma form requires short continuous isotactic sequences in the main chain, whereas very long continuous isotactic sequences generally crystallize in α form\(^ {81}, 82\). The average length of isotactic sequences is inversely related to the content of insertion errors\(^ {80}\). As a consequence, even an overall defect content as low as 0.41mol % reduces the average length of continuous isotactic sequences inducing the crystallization of the γ form\(^ {83}\). The metallocene catalyzed LCB and linear samples chosen for the present study have overall defect content ranging from 1-1.3 mol% thus it is expected that they will exhibit considerable amounts of gamma in a similar temperature range. The LCB samples have an additional contribution to the overall defect content because of the addition of branch points in an otherwise linear isotactic polypropylene. As a result it will be of interest to note the influence of the LCB junctions, (acting as defects) on the overall gamma content as compared to their linear counterpart. Basically, the distribution of defects influences the average length of the crystallizable (fully isotactic) sequences, which, in turn quantitatively controls the formation of gamma polymorph. Thomann et al\(^ {84}\) suggested that any factor which suppresses chain folding makes the formation of alpha modification difficult, but favors gamma formation. The branch points in a long chain branched isotactic polypropylene will disrupt the isotacticity of the linear chain. This exclusion might lead to a long loop formation thereby suppressing the chain folding and consequently it might promote the formation of gamma phase.

The morphology of the polypropylene crystals can be classified in three distinctly different levels\(^ {85}\). At the first level is the unit cell, which we discussed above (α, β, and γ forms). In a second level there is the morphology at the lamellar scale and a third level of morphology is the spherulitic morphology. Lamella grows from a common origin usually in spheric arrangements. Isotactic polypropylene exhibits a variety of spherulites classified by size, brightness and sign of birefringence.
Studies have shown that isotactic PP’s prepared using metallocene catalysts tend to form a mixture of alpha and gamma phases. This is because in chains of iPP samples prepared with metallocene catalysts the interchain defect composition is uniform and the intramolecular distribution of defects is random, whereas for iPP samples obtained with heterogeneous Ziegler-Natta catalytic systems, the majority of the defects may be segregated (intramolecular defect distribution is blocky) in a small fraction of poorly crystallizable macromolecules, so that much longer, fully isotactic sequences can be produced which eventually crystallize in α form.

The alpha phase of iPP exhibits a lamellar branching that is unique in polymer crystallography. It has been observed that the α-phase crystallizes both from solution and the melt as a three dimensional array of nearly orthogonal 'cross-hatched' lamellar arrangement, the cross hatching in alpha form is obtained by nearly orthogonal α branching developing via homoepitaxial growth from parent lamellae. The γ phase of iPP had remained rather elusive for many years. It is not usually observed as a different phase, but (co)crystallizes with and within the α phase spherulites. The arrangement of chains in γ phase departs from common structures of polymer crystallography, in that the chain axes in the structure are not parallel. Instead, the structure is made up of a succession of bilayers tilted 80° to each other.

It has been documented that both branching and molecular weight influence the morphology of semi crystalline polymers. It has also been reported that high molecular weight polymer lacks well defined supermolecular structure and spherulite formation is rarely observed in their crystallization process, also it is generally observed that the rate of spherulite formation and growth increases with undercooling (i.e. at lower Tc’s). The spherulitic morphology has been studied for long chain branched cis 1,4 polybutadiene. Of particular interest is the observation of 'dwarf' (small) spherulites in the highly branched cis 1,4 polybutadiene sample. These dwarf spherulites stopped growing at a size of several microns and induced new dwarf spherulites along its periphery. The formation of dwarf spherulites appears related to the suppressed growth owing to decreased chain mobility with increasing branching.

1.9 Objective of the present study

The copolymerization of propylene using an isospecific metallocene catalyst with small concentrations of 1,9 decadiene,0-400ppm, leads to isotactic polypropylene with H-type intermolecular linkages, resembling 4 arms chemical crosslinks, and leading to enhanced melt
strength by forming LCB. The samples for the present study include two series of propylene 1,9
decadiene copolymers with different LCB distribution. In one series the average Mw increases
from 150K-300K g/mol proportionally with the increase of diene content, while in the second
series it remains basically constant with diene content, 250K-300K g/mol. Therefore, the
exclusive role of H-linkages or LCB on the crystallization rate can be assessed independent of
the effect of molar mass by studying the samples of series 2, whereas the effect of increase in
Mw due to addition of LCB on the crystallization kinetics can be analyzed studying samples of
series 1. A comparison of the results obtained from analysis of the two series of the samples may
be able to provide better insights regarding the effect of either LCB or molecular weight, or both
combined on the crystallization rate from quiescent melts of iPP. A clear understanding of these
two factors on the quiescent crystallization rate is very important since the past literatures are not
very clear on this issue. Conclusions can not yet be driven. A thorough analysis of the linear
growth rates of the two series of samples will allow us to infer the additional influence of LCB
on the overall defect content.

It will be interesting to note whether the quiescent crystallization rate of these H-linked
iPP decreases with increase in branching (as conventionally observed for copolymers) or if the
effect is opposite and in accordance with those observed for sparsely branched
polycaprolactones\textsuperscript{73} and PET\textsuperscript{72}. Since studies\textsuperscript{37} of the crystallization of some of these long
branched iPP, under the application of shear, indicated an increase of the rate of crystallization
with the addition of diene, it is important to compare the effects of two different crystallization
paths: under application of shear and from quiescent melts. These studies will determine if the
observed enhanced crystallization rate is only due to the impact of shear on chain orientation or
if additional effects, such as a possible difference in entropy of melt, may need to be taken into
account to justify such unusual behavior of enhancement in crystallization rates with increase in
branching of long branched isotactic polypropylenes.

The influence of LCB and molar mass on the zero shear viscosity of the two series of
samples is also determined to confirm whether the addition of LCB affects the mobility of the
molecules and thereby impacts the crystallization rate, as it was shown for polycaprolactones\textsuperscript{73}.

The combined effect of branching and molecular weight on the lamellar and spherulitic
morphology was also studied in the present work. It has been demonstrated from previous
studies that the changes in the polymorphic ratio influence the lamellar morphologies, hence
analyzing the morphology of the samples crystallized at different isothermal crystallization temperatures enabled us to investigate the effect of polymorphic contents on the morphology. The supermolecular structure is also dependent on molecular weight and branching level; however, very few works are currently available regarding the morphology of LCB iPP. A thorough morphological analysis of the two sets of series will provide a better understanding of the effect of LCB on the crystalline morphology of poly(propylenes).
CHAPTER 2
EXPERIMENTAL METHODS

2.1 Molecular characteristics of the H-linked isotactic polypropylenes

Two independent series of isotactic poly(propylene)(iPP) samples are studied. The molecular characteristics of the two series of samples studied in the present work are listed in tables 2.1 and 2.2 respectively. The first column lists the sample designation. The nomenclature of the samples follows a certain convention. For example in HLiPP203K1.18, HL stands for H-type linkages, 203K is the weight average molecular weight and 1.18 is the total defect per 100 monomer units. Both tables list the content of diene added, average molecular masses (Mn, Mw, Mz and Mz+1), and the type and content of the defects present in the chain. Additionally, the tables also list the observed melting and crystallization temperature peaks at 10 °C/min and heat of fusion for all the samples.

The diene (1,9 decadiene) introduces H-linkages and additional branches in the otherwise linear iPP chains. For series 1 (Table 2.1), there is a steady increase of Mw and Mz with the addition of diene. Tm and especially Tc increase with addition of diene; however, the heat of fusion (a measure of crystallinity) remains basically unchanged in the series. The characterization data listed in Table 2, for series 2 show that the average molecular weights (Mn, Mw and Mz) do not follow any specific trend with increasing diene. This feature is an indication of a different distribution of the diene between series 1 and 2.

Therefore, in the present work, the combined effect of H-Linkages and molecular weight on crystallization behavior, polymorphism and morphology can be investigated from the samples of series 1 (table 2.1). In the samples of series 2 (table 2.2) the small variation of the molecular weight allows studying the role of the H-linkages on properties independently from the effect of Mw.

The difference in diene distribution between both series, inferred from the variation of molar mass with increasing diene, is most probably due to the synthetic method. While for series 1 all the chains were exposed to diene from the start of the polymerization and, as a result, the molecular weight increased steadily with increase in diene or branching level; however, in series 2 the diene was introduced selectively, targeted to the lower molar mass end of the distribution of chain length. It is perceived by the synthetic chemists that the final product was a mix of 30% diene containing chains and 70% linear PP chains.
The ppm of diene added was converted to moles of diene per 100 moles of iPP (mol %) from overall mass balance.

### Table 2.1 Molecular characteristics of samples of series 1

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Diene level (ppm)</th>
<th>Mn (g/mol) $\times 10^3$</th>
<th>Mw (g/mol) $\times 10^3$</th>
<th>Mz (g/mol) $\times 10^3$</th>
<th>$M_{Z+1}$ (g/mol) $\times 10^3$</th>
<th>Stereo</th>
<th>Stereog 2,1</th>
<th>Regio 3,1</th>
<th>Diene</th>
<th>Total</th>
<th>Defects (mol %)</th>
<th>Tm (ºC)</th>
<th>Tc (ºC)</th>
<th>AHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>51</td>
<td>150</td>
<td>249</td>
<td>356</td>
<td>0.375</td>
<td>0.89</td>
<td>0.042</td>
<td>0</td>
<td>1.31</td>
<td>151.9</td>
<td>108.3</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>200</td>
<td>52</td>
<td>203</td>
<td>460</td>
<td>845</td>
<td>0.183</td>
<td>0.98</td>
<td>0.017</td>
<td>0.006</td>
<td>1.18</td>
<td>154.7</td>
<td>117.1</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>375</td>
<td>112</td>
<td>276</td>
<td>634</td>
<td>1118</td>
<td>0.277</td>
<td>0.85</td>
<td>0.022</td>
<td>0.011</td>
<td>1.15</td>
<td>155</td>
<td>121.8</td>
<td>103</td>
<td></td>
</tr>
</tbody>
</table>

The effect of external nucleators on the crystalline properties was studied in series 1 by the addition of 0.25 % Millad 3988, or 3,4-dimethyl dibenzylidene sorbitol. This is a well known nucleating agent for iPP.

Schematically the differences in branching distribution between the two series are shown below. Here figure 2.1 represents the geometry of series 1 and figure 2.1 the corresponding to series 2. Notice the difference in content and length of long-branched molecules.

### Table 2.2 Molecular characteristics of samples of series 2

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Diene level (ppm)</th>
<th>Mn (g/mol) $\times 10^3$</th>
<th>Mw (g/mol) $\times 10^3$</th>
<th>Mz (g/mol) $\times 10^3$</th>
<th>Stereo</th>
<th>Stereog 2,1</th>
<th>Regio 3,1</th>
<th>Diene</th>
<th>Total</th>
<th>Defects (mol %)</th>
<th>Tm (ºC)</th>
<th>Tc (ºC)</th>
<th>AHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP291K1</td>
<td>0</td>
<td>149</td>
<td>291</td>
<td>498</td>
<td>0.275</td>
<td>0.792</td>
<td>0.006</td>
<td>1.067</td>
<td>151.3</td>
<td>109.8</td>
<td>99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLIPP275K1.18</td>
<td>50</td>
<td>134</td>
<td>275</td>
<td>470</td>
<td>0.275</td>
<td>0.972</td>
<td>0.015</td>
<td>1.07</td>
<td>151.3</td>
<td>109.6</td>
<td>96.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>100</td>
<td>136</td>
<td>283</td>
<td>493</td>
<td>0.275</td>
<td>0.792</td>
<td>0.003</td>
<td>1.067</td>
<td>152.5</td>
<td>112.1</td>
<td>101</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>200</td>
<td>88</td>
<td>247</td>
<td>461</td>
<td>0.275</td>
<td>0.792</td>
<td>0.006</td>
<td>1.067</td>
<td>151.4</td>
<td>111.1</td>
<td>88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In these schematics the red chains are H-linked molecules and the black ones are unlinked. The long chain branch linkage between two iPP molecules is logically a linear hexamethylene segment.

As indicated previously in this section, addition of diene from the beginning of the polymerization process, such as in series 1, increases the probability of diene linkages in most chains, and has a steep effect on the molecular weight most influenced by chain length (Mw, Mz). In contrast, lack of increase of Mw, Mz with increasing diene in series 2 reflects the preferential diene addition in the shorter chains, a desirable technological practice to avoid unwanted gels in the product.

The branch density, defined as the number of molecules of diene per molecule of polypropylene, produced by addition of diene to linear iPP, is an important parameter to understand the interconnectivity of the chain, and also will give some insights regarding the actual irregularity induced in the linear chain by addition of diene. The branch density is calculated as follows:

As listed in table 1, HLIPP203K1.18 contains 200 ppm of 1,9 decadiene. Assuming the diene is added on weight basis, 200g of decadiene is present in $10^6$ g of propene. However, our aim is to calculate the number of molecules of diene per molecule of polypropylene, therefore the actual weights need to be converted to number of molecules. The molecular weight of 1,9 decadiene is 138g/mol, therefore 200g of decadiene contains, $200/138$, i.e. 1.45 molecules of decadiene. The molecular weight of propene is 42g/mol, therefore $10^6$ g of propene contains,
The number of molecules of diene contained in 1238 molecules of propene (or 1 molecule of HLiPP203K1.18) will give us the desired result, i.e. branch density. Since 23810 molecules of propene contained 1.45 molecules of decadiene, therefore, 1238 molecule of propene will contain 0.075 (1.45×1238/23810 = 0.075) molecules of 1,9 decadiene.

The long branch density per iPP molecule is listed for both series in Table 2.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of diene added (ppm)</th>
<th>Number of molecules of 1,9 decadiene/molecule of polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HLiPP203K1.18</td>
<td>200</td>
<td>0.08</td>
</tr>
<tr>
<td>HLiPP276K1.15</td>
<td>375</td>
<td>0.30</td>
</tr>
<tr>
<td>Series 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>iPP291K1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HLiPP275K1</td>
<td>50</td>
<td>0.05</td>
</tr>
<tr>
<td>HLiPP283K1</td>
<td>100</td>
<td>0.10</td>
</tr>
<tr>
<td>HLiPP247K1</td>
<td>200</td>
<td>0.13</td>
</tr>
</tbody>
</table>
2.2 Sample preparation

2.2.1 Sample preparation for DSC experiments

Thin films of the samples were made from the polymer pellets by compression molding in a Carver hydraulic press at 200°C for 3-4 minutes in a rectangular mould of dimensions 1.5cm×2.5cm×0.05cm. From these films, approximately 5mg of sample were cut to fill the DSC pan covered with a lid.

2.2.2 Sample preparation for Atomic Force Microscopy (AFM) and Optical Microscopy (OM)

PP pellets were placed between two aluminum sheets and heated up to 200°C on a Carver laboratory press under a pressure of 1000 psi for 1 minute, followed by rapidly quenching in water. A micrometer was used to measure the thickness of film. The thickness varied within the range of diameter of spherulites, i.e. between 30-60 microns. These thin films were cut into smaller pieces and were sandwiched between two 15mm rounded glass cover slips before being mounted on the hot stage for the growth rate measurements.

Small pieces of films were cut and were sandwiched between round microscopic slides in order to prepare samples for morphological studies by AFM. The microscopic slides were then placed in evacuated tubes and subsequently melted in a silicone oil bath at 200°C for 15-20 minutes and then quickly transferred to a second silicone oil bath maintained at the required crystallization temperature. After required crystallization time had elapsed, the tubes were quenched into a water bath, samples were removed after cooling them to ambient conditions. The cover slips were easily separated by dipping in liquid nitrogen for few seconds to ensure no damage is done to the surface of the samples for subsequent examinations.

2.2.3 Sample preparation for Wide Angle X-ray Scattering (WAXS)

All samples were isothermally crystallized from the melt. A rectangular mould of dimensions 1.5cm×2.5cm×0.05cm was used to prepare polymer films for X-ray analysis. The specimens contained in the mold were sealed in evacuated glass tubes (to prevent degradation and contamination of the samples with the silicone oil used) and melted at 200°C for 15 min. The glass tube containing the samples was then was rapidly transferred to a silicon oil bath set at the required temperature controlled with precision of 0.5°C. The samples were kept immersed in the
oil bath for sufficient time to ensure complete crystallization. The square piece was then taken out of the mold (dimensions 1.5cm×2.5cm×0.05cm) and used for WAXS studies.

2.2.4 Sample preparation for Dynamic Mechanical Analysis (DMA)

Thin films of the samples were made from the polymer pellets by compression molding in the carver press at 200°C for 3-4min in a rectangular mould of dimensions 1.5cm×2.5cm×0.05cm. These films were crystallized in the press (the film was kept in between the two plates with no applied pressure) by slowly cooling down the press to room temperature. A thin strip of dimension 1.5cm×0.5cm×0.05cm was cut from the film and was taken for dynamic mechanical measurements.

2.2.5 Sample preparation for $^{13}$C Solid State Nuclear Magnetic Resonance (NMR)

A rotor of diameter 2.75mm and height 1.5cm was used to pack the polypropylene samples for conducting the solid state NMR experiment. Approximately, 0.8g of sample (pellet) was weighed. A thin film of thickness ~0.3mm was made by compression molding in the carver press at 200°C for 1-2min between two aluminium foils. The entire film was cut into small pieces using scissors in order to pack it tightly and uniformly inside the rotor. The rotor was fitted with a cap before placing it inside the NMR probe.

2.2.6 Sample preparation for Rheology

Small disks of the samples were made from the polymer pellets by compression molding in a Carver press at 200°C for 3-4min in a circular mould of diameter 20mm and thickness 1mm. These disks were sandwiched between two parallel plates in the rheometer.

2.2.7 Sample preparation for FTIR (Fourier Transformed Infra Red Spectroscopy)

Thin films were prepared by placing one single PP pellet between two aluminum sheets and heating it up to 200°C on a Carver laboratory press under a pressure of 1000 psi for 1 minute. The film thickness varied between 20-30 microns. These films of diameter 2cm (apprx) and thickness ~20microns were crystallized in the press (the film was kept in between the two plates with no applied pressure) by slowly cooling down the press to room temperature.
2.3 Characterization techniques

2.3.1 Differential Scanning Calorimeter (DSC)

Melting temperature (Tm), crystallization temperature (Tc) and heat of fusion were obtained in a Perkin Elmer DSC 7 using Pyris software.

To obtain the overall crystallization rates, the samples were isothermally crystallized between a certain range of temperature. The optimum temperature range was chosen between 120-132°C, as below this temperature the crystallization was too fast to be measured by DSC, whereas, above this the crystallization was considerably slow. The crystallization was too fast to observe in DSC at temperatures below 120°C, as the $t_{1/2}$, i.e. the time required to attain half of the transformation, as measured in DSC for HLIPP276K1.15 was 0.2 minutes at 120°C, any time below that would result in a crystallization before steady state is reached at that; whereas above 132°C the crystallization was considerably slow, the $t_{1/2}$ for IPP150K1.31 was ~100 minutes at 132°C. The samples were melted at 200°C for 3 minutes and cooled to the required crystallization temperature at 40°C/min, after the required crystallization time had elapsed, they were melted at 10°C/min from the crystallization temperature. The optimum crystallization time at any temperature was obtained by crystallizing the sample with increasing times and measuring the resulting melting enthalpy. The time after which a constant enthalpy of melting is reached is taken to be the optimum crystallization time required for complete crystallization at that temperature. The overall crystallization rates were obtained from the exothermic DSC peaks as the inverse of the time required to attain half of the transformation.

The DSC was also used to determine the crystallinity level of the samples, based on the enthalpy of fusion measurements. The mass fraction degree of crystallinity $(1-\lambda)\Delta H$ obtained from the enthalpy of fusion is defined as, $(1-\lambda)\Delta H = \Delta H/\Delta H_u$ (2.1)

Here, $\Delta H$ is the measured specific enthalpy of fusion, and $\Delta H_u$ is the enthalpy of fusion per mol of repeating unit of the infinite size perfect crystal, the value of $\Delta H_u$ for isotactic polypropylene used is 209 J/g.93

In DSC the sample and the reference are each provided with individual heaters. It uses the null balance principle, (as quoted from Mcnaughton et. al.94) “the system is divided into 2 loops, the first loop is for average temperature control, so that the temperature Tp, of the sample and the reference may be increased at a predetermined rate, which is recorded. The second loop
ensures that if a temperature difference develops between the sample and the reference the power input is adjusted to remove this difference.”

The sample is encapsulated in an aluminum pan with a lid. To ensure optimum peak resolution the contact surface between the pan and sample should be maximized. For calibration of the instrument, high purity materials with accurately known enthalpies of fusion are used (Indium is one of the most commonly used metals for calibration). When a sample material is subjected to a linear temperature increase, the rate of heat flow into the sample is proportional to its instantaneous specific heat. Comparing this heat flow with a standard material under the same condition, the specific heat Cp as a function of temperature can be obtained.

To calculate Cp the empty aluminum pans are kept in the sample and reference holder, an isothermal base line is recorded at both lower and higher temperature, these two base lines are used to create a base line over the scanning zone. This procedure is then repeated with a known mass of sample and \( \frac{dH}{dT} \) is recorded against time, there will be displacement due to absorption of heat. The following equation (2.2) is used to obtain Cp,

\[
\frac{dH}{dT} = mCp \frac{dT_p}{dt},
\]

where, \( m \)=mass of the sample in grams, \( Cp \)=specific heat cal/g

\( \frac{dT_p}{dt} \)=programmed rate of temperature increase.

In cases (such as for polymers) where there is little or no change in heat capacity before and after a transition, the enthalpy changes (\( \Delta H \)), can be isolated from the heat capacity\(^1\).

2.3.2 Solid State Nuclear Magnetic Resonance

Room temperature spin-lattice relaxation times (\( T_{1C} \)) were measured using a saturation recovery cp MAS (cross-polarization-magic angle spinning) method. The solid state NMR experiment was carried out on Bruker DMX300 spectrometer operating at 75.5 MHz for \(^{13}C\). The experiments were conducted using a Bruker solid state probe for 7mm rotors. The MAS frequency was 3000 ±500 Hz. A contact time of 500µs was used in the cp MAS experiments. Signal averaging was collected using 27 different delay times ranging from 100 miliseconds to 7 seconds.
The nuclei of all elements carry a charge. When the spins of the protons and neutrons
comprising these nuclei are not paired (\(^{1}\text{H}\), \(^{13}\text{C}\), \(^{15}\text{N}\), \(^{19}\text{F}\) etc), the overall spin of the charged
nucleus generates a magnetic dipole along the spin axis, and the intrinsic magnitude of this
dipole is a fundamental nuclear property called the nuclear magnetic moment, \(\mu\). When this
vector is placed in an external magnetic field, it divides itself into \(2I+1\) energy levels. For proton
or carbon 13, nuclear spin number \(I\), is \(\frac{1}{2}\), and the application of magnetic field separates the
nuclear levels into two. The relationship ruling the separation is given by equation (2.3):
\[
\Delta E = h\gamma B_o,
\]  
(2.3)
\(\Delta E\) = energy gap, \(\gamma\) = gyromagnetic ratio, \(B_o\) = External magnetic field.

Brief radio frequency (rf) pulses are used to excite the spins in an NMR environment.
These pulses rotate the net magnetization vector about the axis of applied pulse and generate a
torque on the net magnetization vector. The process by which the spins that were excited in a rf
pulse returns to their equilibrium population distribution is called relaxation.

The spin lattice relaxation governs the return of \(z\) magnetization to their equilibrium
value, in this process the spin system gives its excess energy to its surrounding, “lattice”. Spin
lattice relaxations are sensitive probe of molecular motion within a molecule, and the time taken
for relaxation can tell us whether a given chemical environment is in a rigid or flexible portion of
the molecule. Large differences in the molecular dynamics between the crystalline and the
amorphous phases make it easier to distinguish between the phases, as they have very different
relaxation times.

Mathematically, the time dependency of the macroscopic magnetization \(M\) is described
by the Bloch equation:
\[
\frac{dM_z}{dt} = -\frac{1}{T_1} (M_z - M_0)
\]  
(2.4)
integrating over \(0\) to \(t\) gives:
\[
M_z = M_0 (1 - e^{-\frac{t}{T_1}})
\]  
(2.5)
In this equation, \(M_z\) is the magnetization at time \(t\), and \(M_0\) the magnetization at equilibrium or
the final intensity value. \(T_1\) is the spin lattice relaxation time, which is essentially is a measure of
the driving force, the displacement from equilibrium, returning the spin system to its equilibrium.
There are several nuclear-spin interactions, namely chemical shifts, dipolar and scalar interactions which could affect the lineshape of the spectrum. These interactions comprise the sources of broadening in $^{13}$C spectra of organic solids. Chemical shift depends on the extent to which the surrounding electrons shield or deshield the nucleus from the external magnetic field. The chemical shift can be written as follows:

$$\delta (\phi) = \langle \delta \rangle + 1/3(\delta_{\|} - \delta_{\perp})(3\cos^2 \phi - 1)$$

(2.6)

$\phi$ is the angle that the axis of the carbon makes with $B_O$. $\delta_{\|}$ and $\delta_{\perp}$ are the chemical shifts corresponding to $\phi$ at zero and $90^\circ$ angles respectively. $\langle \delta \rangle$ is the isotropic shift observed in solution and the next term is the anisotropic part of the chemical shift.

The removal of broad dispersion due to chemical shift is achieved by magic angle spinning (MAS). The sample is mechanically spun with respect to an axis at an angle of 54.74° (magic angle) with respect to the magnetic field direction, this helps in averaging the anisotropic part of the shift once the rotation rate is greater than the chemical shift anisotropy.

In solids, the molecular motion is limited and this leads to very inefficient spin lattice relaxation. For C-13 nuclei the correlation time is very long (especially for methine and methylene groups in polypropylene, as methyl group rotate rapidly and have lower $T_1$) and even though protons on methyl carbons do communicate their short $T_1$ to other protons in the sample via diffusion to nearby spins, these protons cannot communicate their $T_1$ back to other carbons in the sample since the carbons and protons resonate at very different frequencies. Cross polarization takes advantage of the fact that proton spin diffusion is shorter than carbon and all the protons in a sample usually have same $T_1$ value. In cross polarization (CP) an overlap of proton and carbon energies occur, and, proton spins are locked in the rotating frame followed by switching on $^{13}$C field with the amplitude satisfying Hartmann-Hahn condition

$$\gamma_c B_{1C} = \gamma_H B_{1H}$$

(2.7)

where $\gamma$’s are the respective gyromagnetic ratios and B’s are the corresponding radio frequency amplitudes. When the proton and carbon energy levels match, polarization is transferred from the abundant protons to the rare carbon-13 nuclei. Therefore, the shorter $T_1$ of the proton dictates the repetition rate for signal averaging.
2.3.3 Wide Angle X-ray Scattering (WAXS)

Wide Angle X-ray Scattering (WAXS) or Wide Angle X-ray diffraction (WAXD) is a technique that is often used to determine the crystalline structure of polymers. This technique specifically refers to the analysis of the peaks that lie in a wide range of angles, which (by Bragg's law) implies that they are caused from diffraction of the X-ray by sub-nanometer sized structures. The polymers form stacks of lamella on crystallization from either melt or solution. The stack scatters X-rays in a similar way to the atoms in a crystal lattice and Bragg’s law is obeyed.

\[ n\lambda = 2dsin\theta \]  

(2.8)

where \( n \) is an integer, \( \lambda \) is the wavelength of the radiation, \( d \) is the periodicity of the array and \( \theta \) the diffraction angle.

The technique can be used for determination of degree of crystallinity of polymer samples. The diffraction pattern generated allows determination of the phase composition of the film, the texture of the film (preferred alignment of crystallites), the crystallite size. According to this method the sample is scanned in a wide angle X-ray goniometer, and the scattering intensity is plotted as a function of the \( 2\theta \) angle. When X-rays are directed in solids they will scatter in predictable patterns based upon the internal structure of the solid. A crystalline solid consists of regularly spaced atoms (electrons) that can be described by imaginary planes. The distance between these planes is called the d-spacing. The intensity of the d-space pattern is directly proportional to the number of electrons (atoms) that are found in the imaginary planes. Every crystalline solid has a unique pattern of d-spacings, which is a “finger print” for that solid. In fact solids with the same chemical composition but different phases can be identified by their pattern of d-spacings.

In the present study room temperature WAXS diffractograms were obtained using a slit collimated Siemens D-500 diffractometer in a \( 2\theta \) range between 5º and 40º with a step size of 0.02º. The diffractometer operated at 30mA and 40kV.

The WAXD method used in this work to determine the degree of crystallinity, involves the analysis of a set of discrete crystalline reflections (Bragg spacings) that are superposed upon a broad amorphous halo. A representative example is given in Figure 2.3. To calculate crystallinity, it is necessary to separate, or deconvolute, the amorphous halo from the crystalline reflections. Following the work of Alamo, et. al.⁹⁷, hydrogenated poly (2-methyl-1,3-pentadiene)
was chosen as the atactic completely amorphous sample. As seen in the figure, the WAXS pattern of this atactic polymer (red curve) was superimposed upon the diffraction pattern of the semicrystalline iPP. The crystallinity was calculated after subtracting the area of the amorphous WAXS pattern \( A_A \) from the total intensity of the iPP diffractogram \( A_T \). The result is shown in figure 2.4. The degree of crystallinity is calculated as:

\[
X_c = \frac{A_T - A_A}{A_T}
\]  

(2.9)

**Figure 2.3** WAXD Diffractogram of HLiPP276K1.15 crystallized at 140°C and amorphous halo (red curve)
At the level of the unit cell, isotactic polypropylene (iPP) exhibits three different morphological forms, $\alpha$, $\beta$ and $\gamma$, distinguished by the arrangement of the chains. Each of these forms is identified with specific peaks in the X-ray pattern (refer to the section on polymorphic behavior in chapter 3). The samples for the present study crystallize exclusively in alpha and gamma form (a characteristic of metallocene catalyzed iPP with defects). Here, the fractional content of gamma phase was obtained from the height of the $(117)$ reflection at $2\theta = 20.1^\circ$, characteristic of gamma form and the $(130)$ reflection at $2\theta = 18.8^\circ$, typical of the alpha polymorph, as $H_\gamma/H_\gamma+H_\alpha$. The fraction of the $\gamma$-phase was obtained from the diffractograms at room temperature, following different methods (the details are given later in the section of polymorphic behavior in chapter 3). The description of one of the method given by Turner-Jones$^{98}$ is detailed in this section. Here, the fractional content of gamma phase was obtained from the height of the $(117)$ reflection at $2\theta = 20.1^\circ$, characteristic of gamma form and the $(130)$ reflection at $2\theta = 18.8^\circ$, typical of the alpha polymorph, as $H_\gamma/H_\gamma+H_\alpha$.

An example is shown in figure 2.5 for the sample HLiPP203K1.18 at aTc of 130°C.

Figure 2.4 Diffractogram of pure crystalline phase of HLiPP276K1.15, after subtraction of the amorphous portion.

![Diffractogram of pure crystalline phase of HLiPP276K1.15, after subtraction of the amorphous portion.](image-url)
2.3.4 Optical Microscopy (OM)

Optical Microscopy was used to study the nucleation density, spherulitic morphology and linear growth rates of the poly(propylenes) of interest. The properties were measured (linear growth rate and nucleation density) and studied (morphology) using an Olympus BH-2 optical microscope fitted with an Olympus DP/2 digital camera and a Linkam hot stage TP-93. The temperature was controlled with a precision of ± 0.1°C. The diameter of a spherulite is measured using a graduated microscope eyepiece calibrated by a standard micrometer. Linear growth rates were obtained from the slope of the linear plots of the spherulitic radius against time. As an example, the change in the radius of the spherulite, measured as a function of time at different Tc’s for IPP150K1.31 is displayed in figure 2.6. A film of polypropylene was sandwiched between two cover slips and heated to 200°C. The cover slip was pressed slightly for 10 seconds to make the melt homogeneous and free of air bubbles. The sample was then kept at that temperature for 3 min to erase melt memory effects and further cooled at 40°C/min from the melt to the isothermal crystallization temperature. The choice of the cooling rate is based on the

---

Figure 2.5 The WAXD diffractogram of HLIPP276K1.15 at 140°C is shown. The fractional content of gamma phase was obtained from the height of the reflection at 2θ (Hγ) = 20.1°, characteristic of gamma form and the reflection at 2θ = 18.8°, typical of the alpha polymorph (Hα), as, gamma content = Hγ/(Hγ+Hα). (Turner-Jones method)
following: we observed that at cooling rates below 40°C/min the sample crystallizes partially before reaching the desired crystallization temperature. Conversely, cooling rates above 40°C/min are too fast for the temperature monitoring system and temperature readings will not reflect the true value due to limitation of effective heat transfer. Once the sample reached the desired Tc, the change in the radius of spherulite with time was measured and recorded.

![Graph showing linear growth rate for IPP150K1.31 at indicated crystallization temperatures.](image)

**Figure 2.6** Representative data of linear growth rate for IPP150K1.31 at the indicated crystallization temperatures.

### 2.3.5 Atomic Force Microscopy (AFM)

The lamellar morphology was studied using AFM. AFM images were obtained using a Jeol 4210 scanning probe microscope. The software allows collection of topography and phase images in non-contact (tapping) AC mode. Images were obtained using Olympus single side coated silicon cantilevers with a resonant frequency ~300Khz.

Some of the advantages of this technique include high resolution, non-destructive and easy sample preparation. Tapping mode is generally utilized for studying polymer surfaces using
AFM. When operated in air or other gases, the cantilever is oscillated at its resonant frequency and positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. In the very short time over which this contact occurs, the lateral forces are dramatically reduced as the tip scans over the surface. When imaging poorly immobilized or soft samples, tapping mode may be a far better choice than contact mode for imaging. If the tip were scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube, that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. The Laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector whose output signal is collected by differential amplifier. The height image data (topography) obtained by the AFM is three-dimensional. The usual method for displaying the data is to use different color or shade to distinguish the difference in height of the features, for example darker shades are used for low features and lighter shades are used for high features.

One development in tapping mode is the use of the changes in phase angle of the cantilever probe to produce a second image, called a phase image or phase contrast image. This image often provides significantly more contrast than the topographic image and has been shown to be sensitive to material surface properties, such as stiffness, viscoelasticity, and chemical composition. In general, changes in phase angle during scanning are related to energy dissipation during tip-sample interaction and can be due to changes in topography, tip-sample molecular interactions, deformation at the tip-sample contact, and even experimental conditions. Depending on the operating conditions, different levels of tapping force might be required to produce accurate, reproducible images on different samples.

2.3.6 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical relaxation spectrum of the sample was obtained using a TA Instruments DMA 2980 analyzer. Dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA) is most useful for observing the viscoelastic nature of polymers. An oscillating force is applied to a material and the resulting displacement of the sample is measured. This method is the most commonly used one today. Samples can be either solids or
melts. Most solids are tested by linearly applied strains and melts or liquids are normally tested in shear. From dynamic mechanical analysis the stiffness of the sample can be determined, and the sample modulus can be calculated. By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. The time lag is reported as a phase lag, which is an angle. The damping is called tan delta, as it is reported as the tangent of the phase lag. Viscoelastic materials (such as polymers) typically exist in two distinct states. They exhibit the properties of a glass (high modulus) at low temperatures and those of a rubber (low modulus) at higher temperatures. By scanning the temperature during a DMA experiment this change of state (the glass transition), can be observed. The glass transition temperature (Tg) is often measured by DSC (Differential Scanning Calorimetry), but the DMA technique is more sensitive and yields more easily interpreted data. DMA can also resolve transitions below Tg in many materials that the DSC technique is not sensitive enough to pick up, like gamma transition in iPP. In addition, DMA gives modulus values.

A thin strip was cut from the film (as discussed in sample preparation for DMA) and was taken for dynamic mechanical measurements. The measurements were run from –80 to 160°C at a heating rate of 2°C/min and a frequency of 1Hz.

2.3.7 Shear Rheometer

The shear rheology was studied using a Rheometrics Scientific Advanced Rheometric Expansion System (ARES) at University of Tennessee, Knoxville. The rheometer is used for dynamic or constant rotational operation and is capable of operating in either a controlled stress or controlled strain mode. Normal forces can be measured in constant rotation. The parallel-plate geometry was used with plates with a 20-mm diameter and a 1-mm gap. The rheological experiments were conducted at 210°C in a frequency range from 0.1 rad/s to 100 rad/s.

In a parallel plate rheometer the polymer is placed between the two plates, as the temperature is raised beyond the polymer melting point, the polymer becomes liquid. One of the two plates can be rotated or oscillated. The instrument measures the torque, M required to separate the two plates when the gap between them is maintained fix. The shear stress, τ, is expressed as
\[
\tau = \frac{3M}{2\pi R^3} \left[ 1 + \frac{d \ln M}{3d \ln \gamma(R)} \right]
\] (2.10)

R is the radius of the plate and \( \gamma \) is the shear rate given as, \( \gamma = \omega R/h \), where h is the vertical gap between the two plates and \( \omega \) is the rate of angular rotation.

In order to get the shear stress at a single value of shear rate, the torque have to be measured at several values of shear rate and differentiate the data; the data can be collected by varying the speed of angular rotation. The dynamic viscosity, \( \eta \), is given as \( \eta = \tau/\gamma \). Thus by from the ratio of shear stress and shear rate we can easily obtain the viscosity.

In small amplitude sinusoidal deformation with an angular velocity of \( \phi_0 \) such that entire sample is within linear viscoelastic region, a measurement of the torque amplitude \( M_0 \) and its phase difference \( \delta \) with the angular deformation yields;

\[
G' = 2 M_0 h \cos \delta/\pi R^4 \phi_0
\] (2.11)

\[
G'' = 2 M_0 h \sin \delta/\pi R^4 \phi_0
\] (2.12)

The storage modulus, \( G' \) is defined as component of the stress in phase with strain divided by the strain amplitude and the loss modulus, \( G'' \) is defined as component of the stress out of phase with strain divided by the strain amplitude. The ratio of the loss modulus to storage modulus is defined as \( \tan \delta \), and is an alternate measure of energy dissipation in viscoelastic materials.

2.3.8 FT-IR

The IR spectra were recorded at a resolution of 4.0 cm\(^{-1}\) at room temperature using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. After background subtraction, the spectra were collected in absorbance mode. Infrared spectra can be very instrumental in determining the degree of crystallinity.

The crystallinity of iPP is determined by analysis of the FTIR absorbance spectra applying Lambert and Beer’s law to selected peaks. Lambert Beer law is an empirical relationship that relates the absorption of light to the properties of the material through which the light is traveling (equation 2.13)

\[
A = \alpha l c
\] (2.13)
Where,

\( A \) = is the absorbance of the sample \\
\( \alpha \) = is the absorption coefficient \\
\( l \) = is the distance that the light travels through the material \\
\( c \) = is the concentration of absorbing species in the material

Lamberti et al. applied this law to a crystalline and a reference peak assuming that the absorbance of both the amorphous and crystalline phases does not depend on phase-content distribution. Accordingly the law provided,

\[
A_{cr} = a_{cr}X_cS \\
A_r = a_rS
\]

Equation 2.13 and 2.14 for the crystalline and reference peak respectively.

In the above equations, \( A_{cr} \) and \( A_r \) are the absorbance of the crystalline and reference peaks, \( X_c \) is the crystallinity and \( S \) is the sample thickness.

Eliminating \( S \) from equation 2.14 and 2.15,

\[
X_c = a_r A_{cr}/A_r a_c
\]

With eq 6, crystallinity evaluation requires only absorbance measurements (\( A_{cr} \) and \( A_r \)) if the absorption coefficients ratio (\( a_r/a_{cr} \)) is known.

The absorbance peak at wavenumber 841 cm\(^{-1}\) for iPP was identified in literature\(^99\) and experimentally as a crystalline peak and the absorbance peak at 973 cm\(^{-1}\) was used as internal standard, being a peak essentially insensitive to structure i.e. to amorphous crystalline ratio. To obtain the value of absorptivity ratio a comparison of results from WAXS and FTIR was carried out on the basis of total crystalline content. The numerical value of absorptivity ratio was found to be \( a_{973}/a_{841} = 0.79^{100} \).

The peak at 973 cm\(^{-1}\) is assigned to the rocking mode of CH\(_3\) group and assymetric stretching of C-C bond, \([r(CH_3)\) and \(\nu_b(CC)\) respectively]. This vibration mode is used as internal standard because the intensity of this peak does not change appreciably with crystallization or melting. The intense band at 841 cm\(^{-1}\) disappears or decreases in intensity during melting of IPP or with decrease in stereoregularity, therefore, that peak was identified as a crystalline peak and is assigned to a CH\(_2\) rocking mode, \(r(CH_2)\).
The IR absorbances for the samples of the two series were measured in a range of 500 – 4000 cm\(^{-1}\) wavenumber. An example of the spectra is shown below in figure 2.7.

Figure 2.7. IR absorbance spectra of IPP150K1.31

Figure 2.8 Crystalline (cr) and reference (r) peaks in IR absorbance spectra of IPP150K1.31
The absorbance of the crystalline ($A_{cr}$) and reference ($A_r$) peaks were obtained from the peaks at 841 cm$^{-1}$ and 973 cm$^{-1}$ respectively of figure 2.7. In order to identify the crystalline and reference peak better, Figure 2.8 is obtained by magnifying figure 2.7 between wavelength 800-1000 cm$^{-1}$, and absorbance 0-0.8. The crystallinity, $X_c$ can subsequently be calculated by means of equation (2.16), taking the value of absorptivity ratio as 0.79.
CHAPTER 3
RESULTS AND DISCUSSIONS

3.1 Crystallization behavior

3.1.1 Cooling/heating at 10°C/min

Non isothermal crystallization and melting behavior of both series were initially evaluated to test the difference in thermal properties with the addition of diene. Thermograms (exotherms and endotherms) obtained upon dynamic heating and cooling of the samples at 10°C/min are shown below in figure 3.1. The peak crystallization temperature, Tc, increases from 108 to 121°C for series 1 with 0 to 375 ppm of diene addition, whereas for series 2 the difference in peak Tc between linear and diene contained sample is substantially less, and only an increase of 2°C is observed on addition of 200pm decadiene. Tables 3.1 and 3.2 display the Tm, Tc and heat of fusion values of the samples of series 1 and 2 respectively. Since LCB is present in the longer chains of the first series and not in the long chains of the second (refer to molecular characteristics of the samples in experimental section), the non-isothermal data infer that the longer molecules with higher contents of LCB are responsible for the observed increase.

The close proximity of the melting temperatures (Tm) of linear and branched iPPs in series 2 can be explained from the overall defect content of the samples. A slight increase (2-3°C) in melting temperatures of diene contained samples in series 1 is a consequence of the increase in Tc due to nucleation difference, which will be addressed in a subsequent section. Since melting temperature is a function of the overall defect content, then it can be stated that on account of the similar overall defect content of iPPs in each series, there is little difference in their melting points. The wider difference in the peak crystallization temperatures (~15°C for series 1) could be a consequence of a difference in the nucleation density of the samples.

The heat of fusion values of the diene contained sample are similar to that of the linear one in both series. This indicates that the incorporation of diene has not altered the crystallinity of the linear iPP.
Table 3.1 Peak transition temperatures for samples of series 1 obtained at 10°C/min

<table>
<thead>
<tr>
<th>Samples</th>
<th>Diene (ppm)</th>
<th>Tm* (ºC)</th>
<th>Tc* (ºC)</th>
<th>ΔHm* (J/g)</th>
<th>Overall Defects (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>151.9</td>
<td>108.3</td>
<td>101</td>
<td>1.31</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>200</td>
<td>154.7</td>
<td>117.1</td>
<td>107</td>
<td>1.18</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>375</td>
<td>155.0</td>
<td>121.8</td>
<td>103</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 3.2 Peak transition temperatures for samples of series 2 obtained at 10°C/min

<table>
<thead>
<tr>
<th>Samples</th>
<th>Diene (ppm)</th>
<th>Tm* (ºC)</th>
<th>Tc* (ºC)</th>
<th>ΔHm* (J/g)</th>
<th>Overall Defects (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP291K1</td>
<td>0</td>
<td>151.3</td>
<td>109.8</td>
<td>99</td>
<td>1.07</td>
</tr>
<tr>
<td>HLIPP275K1</td>
<td>50</td>
<td>151.3</td>
<td>109.6</td>
<td>96.6</td>
<td>1.07</td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>100</td>
<td>152.5</td>
<td>112.1</td>
<td>101</td>
<td>1.07</td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>200</td>
<td>151.4</td>
<td>111.1</td>
<td>88</td>
<td>1.07</td>
</tr>
</tbody>
</table>

*Tm= Melting temperature, Tc= Crystallization temperature and ΔHm = Heat of fusion

Figure 3.1 DSC Melting (a, c) and Crystallization (b, d) thermograms of series 1 and 2, obtained at 10°C/min
3.1.1.2 Difference in nucleation density upon crystallization from quiescent melt

The samples of series 1 have similar overall defect content. However, in the previous section we observed that for samples of series 1 the $T_c$ (crystallization at 10°C/min) increases with increase in diene addition, suggesting an increase in overall crystallization rate. An increase in the nucleation density on addition of diene could be a possible reason for the above observation.

The nucleation densities of the specimens were studied using optical microscopy. The optical micrograph images (figure 3.2 and 3.3 for series 1 and 2 respectively) confirm that the H-linked samples have considerably higher nucleation densities compared to the linear one at a fixed crystallization temperature. The difference in crystallization temperature for the samples of series 1 correlates with the observed difference in the nucleation densities of the samples.
Figure 3.2  Polarized optical micrographs of iPP (series 1) with increasing contents of diene at a crystallization temperature of 130°C for (a) 5 min, (b) 1 min and (c) 45 sec.

An optimum Tc of 130°C was chosen so that the initiation of the spherulites could be captured in the optical microscope, the nucleation was too fast below that temperature and was much delayed for the linear above it. For the samples of series 1 the nucleation density was observed to directly depend on the addition of diene, whereas when the diene was targeted to the chains of low molecular weight, the nucleation density did not appear to directly depend on either diene content or molar mass. As is observed in figure 3.3c, the sample with intermediate diene content (HLIPP283K1, 100ppm diene) has the highest nucleation density. Therefore, as opposed to the trend followed for samples in series 1 any correlation of nucleation density with diene content or molar mass can be ruled out for the samples of series 2 with a different distribution of diene molecules along the iPP backbone.
Figure 3.3 Polarized optical micrographs of iPP (series 2) with increasing contents of diene at a crystallization temperature of 130°C for (a) 3.3 min, (b) 3.1 min, (c) 2.2 sec and (d) 3.2 min.

An attempt was made to quantify the difference in nucleation density (comparing the linear one with the H-linked) for the series 1 samples but the enormous nucleation density of the H-linked samples (figure 3.2) resulted in the formation of tiny and numerous nuclei and made it impossible to account for the total number of nuclei in the micrographs. The nucleation densities of the second series were also studied and quantification of the nucleation density was possible, an increase of 400% in the nucleation density on addition of 200 ppm diene to the linear sample was observed, as shown in figure 3.4. Hence, it is the nucleation density what is enhanced by the addition of small contents of LCB to the iPP chain, especially when added to the longest chains.
3.1.1.3 Crystallization after reprecipitation from solution

In case of heterogeneous nucleation, the presence of catalyst and co-catalyst residues may cause an increase in the nucleation density since they provide an already existing surface from where nuclei can form and grow into crystals. To probe this possibility we attempted to eliminate the residues of co-catalyst by dissolution and reprecipitation of the polymers of the first series. Once reprecipitated, the samples were dried and crystallized under identical condition as the original ones to observe (with the help of optical microscopy) whether there is any difference in the nucleation activity owing to possible influence of co-catalyst residues.

Methylaluminoxane (MAO) is the co-catalyst used alongwith metallocene catalyst. Since xylene is a solvent for MAO, the samples were first dissolved in hot xylene at 130°C in an attempt to remove the possible residues of the co catalyst, and then were precipitated by adding excess methanol. The filtrate was washed several times with methanol and then dried to obtain the samples in powdered form. Thin films of the samples were made using a hot press. Similar to previous section (3.1.1.2), a thorough observation of the initiation of spherulites from an optimum Tc was recorded. The comparison of nucleation densities of the solution treated linear and H-linked samples will allow us to determine whether an excess amount of co catalyst was used for the production of H linked samples that was responsible for enhanced nucleation
activity, or whether an intrinsic difference in chain architecture led to such different nucleation between linear and H-linked isotactic polypropylenes.

Nucleation density of the solution treated samples (series 1) is compared with the original ones under identical conditions in figure 3.5. Minimal variation of nucleation density between the original and solution treated samples is apparent from the optical micrographs as a result the possibility that the impurities were causing the observed increase in nucleation density in the original samples can be ruled out, since, if excess co catalyst was present in the H-linked samples then the nucleation density of the solution treated samples, devoid of co catalyst, would have been significantly lower than the original ones (as xylene would have dissolved the co catalyst). To further confirm the effect of co catalyst on thermodynamics of crystallization, the Tm and Tc of the solution treated and original samples were compared. The comparison of thermal properties is listed in table 3.3. The Tm, Tc and heat of fusion of the solution treated H-linked samples are slightly (~3°C) lower than the original ones, this may be attributed to the presence of solvent residues in the former samples.

Table 3.3 Comparison of thermal properties of original and solution treated samples of series 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene (ppm)</th>
<th>Type</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>ΔHm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>Original</td>
<td>151.9</td>
<td>108.3</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution treated</td>
<td>152</td>
<td>108.8</td>
<td>95.3</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>200</td>
<td>Original</td>
<td>154.7</td>
<td>117.1</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution treated</td>
<td>152.2</td>
<td>113.9</td>
<td>89.8</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>375</td>
<td>Original</td>
<td>155</td>
<td>121.8</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solution treated</td>
<td>152</td>
<td>118.1</td>
<td>86.9</td>
</tr>
</tbody>
</table>
In order to find out whether the solution treated samples gathered some impurities during the process, the linear growth rate of the solution treated samples were compared to that of the original ones at certain isothermal crystallization temperatures. In figure 3.6 the growth rate of the solution treated samples of series 1 are indicated with open symbols along with the solid black line indicating growth rate trend of each of the original samples. The details of the growth rate analysis of original samples of series 1 are shown later in section 3.1.2.5. It is clear in this that there is no change in the growth rate of the solution treated and the original samples of series
1 in the range of Tc studied, therefore the speculation that the solution treated might contain impurities can be ruled out.

![Graph](image)

**Figure 3.6** Linear growth rate of the solution treated samples. The solid black lines indicate the variation of the growth rate of the original samples with Tc. The symbols correspond to the samples recrystallized from solution.

### 3.1.1.4 Crystallization from homogenous melts

Dynamic crystallization at 10°C/min after melting and holding the melt for 3 minutes at 200°C suggested that the H-linked samples crystallize at much faster rate than their linear counterpart (especially samples of series 1). The results also infer that this increase is parallel to the addition of diene.

Owing to the importance of primary nucleation mechanism in determining the overall crystallization rate and morphology during processing of semicrystalline polymers, it is necessary to understand and investigate the influence of impurities, additives, nucleating agents and especially crystalline memory effect (thermal history of the sample) on the crystallization behavior. Sometimes clusters of molecules that retain some of their crystalline arrangements due
to insufficient or partial melting, can act as predetermined nucleation sites on cooling, thus triggering the memory effect. These aggregates can greatly enhance the crystallization rate. To eliminate this effect it is necessary to keep the polymer melt at a sufficiently high temperature for sufficiently long time in order to eradicate the preoriented structures. This effect on syndiotactic polypropylene and polytrimethylene terephthalate has been studied in detail by Supaphol et al. Mandelkern and co workers studied the influence of the melting conditions on the subsequent crystallization behavior for linear PE between an initial melt temperature range of 139-180°C, and, concluded that the crystallization isotherms are quantitatively independent of the precrystallization treatment in the molten state for molecular weights less than $1.2 \times 10^6$ g/mol. For a molecular weight of $8 \times 10^6$ g/mol, the isotherm obtained after the initial melting at 160°C was unusual as it did not fit into any particular pattern with respect to the results for the lower molecular weights. For isotactic polypropylene, Alfonso et. al. studied the crystallization behavior from different initial melt temperatures higher than the apparent melting point. The range of initial melting temperature was 250-290°C. Subsequently, they observed that the initial melt formed by heating to different temperatures (Ts) has different degrees of order, and therefore, the correspondent crystallization behaviors of these melts were different from one another.

The fusion temperature needs to be higher than the equilibrium melting temperature ($T_m^0$) of the specific polymer. There is a controversy regarding the exact value of $T_m^0$ for isotactic polypropylene, values from 186-212°C have been reported in the literature. The fusion temperature that has been used for our study (200°C) is in between the range of $T_m^0$ reported in literature; as a result memory effect could be a possible reason for the observed difference in the rates. Another cause of concern for the difference in rate of crystallization of H-linked samples compared to the linear ones, in addition to melt memory effects, may arise from the existence of some higher thermal stability of mesomorphic phase in iPP. It has also been suggested that the equilibrium melting temperature of a mesomorphic form of iPP may be located at a higher value than that of the crystalline phase; if this is the case, a melting temperature higher than 200°C would be required to ensure melt homogeneity.

In order to rule out the possible influence of melt memory effects or the existence of mesomorphic phase on the crystallization rate and justify that the difference in rate is not a
consequence of either of these phenomenon, the initial fusion temperature and the time for which it is kept at that temperature (initial hold time) must be increased prior to crystallization.

The crystallization parameters (Tc, heat of crystallization) were compared from different initial melt conditions to observe the effect of thermal history on crystallization behavior. In accordance with previous reports\textsuperscript{101, 104}, with increase in initial melt temperature an increase in crystallization half time (or decrease in Tc) is expected if some preoriented structures are formed at lower Tm’s. As long as the effect is similar on all the samples (linear and H-linked), the possible influence of thermal history on enhancing the nucleation specifically of H-linked samples can be ruled out.

Dynamic crystallization at 10°C/min were carried out for samples of series 1 from the following four different conditions:

1) Melt at 200°C and hold for 3min  
2) Melt at 200°C and hold for 10min  
3) Melt at 250°C and hold for 3min  
4) Melt at 250°C and hold for 10min

The thermograms of crystallization from different initial condition (melt temperature and initial holding time) and their subsequent melting peaks are shown respectively for the three samples of series from figure 3.7 - 3.12

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.7.png}
\caption{Crystallization of IPP150K1.31 at 10°C/min (*Indicates the initial fusion temperature and holding time)}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.8.png}
\caption{Melting of IPP150K1.31 at 10°C/min}
\end{figure}
The influence of initial fusion temperature and holding time on the rate of crystallization (Tc) and subsequent melting is evident from the figures; there is a moderate decrease (3-5°C) in the crystallization temperature (Tc) with increase in either the initial fusion temperature or holding time. By increasing the holding time from 3 to 10 minutes at same initial fusion temperature the decrease in Tc is marginal (~1°C), but by changing the initial melting temperature to 250°C from 200°C without changing the hold time, the Tc decreased by at least 3°C for all the samples.
Table 3.4 lists the peak temperatures and the heat of fusion/crystallization for the three samples of series 1 as obtained for each of the thermograms from different initial conditions.

From the data (table 3.4) it is evident that the change in the initial melt temperature and the holding time indeed influenced the crystallization temp (Tc) and subsequent melting point. The peak Tc and melting point is lowered by 3-5°C for each of the samples by changing the initial fusion temperature from 200 to 250°C and increasing the holding time from 3 to 10 minutes.

The most important thing to note is that in all the four different cases (changing the fusion temperature or holding time) each of the three samples are equally affected i.e. the difference between the peak Tc for each sample remain almost the same under a particular set of condition. For example, the Tc is lowered for both the linear and the sample with highest diene by changing fusion temperature from 200 to 250°C and increasing the holding time from 3 to 10 minutes, but the difference in Tc remains the same, i.e. between 14-15°C.

Table 3.4 Peak temperatures and heat of fusion/crystallization for the three samples of series 1 as obtained from different initial conditions

<table>
<thead>
<tr>
<th>Initial Melt Temp (°C)</th>
<th>Holding time (min)</th>
<th>Tc(°C)</th>
<th>ΔH(cryst) (J/g)</th>
<th>Tm(°C)</th>
<th>ΔH(melting) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31-0 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>107.96</td>
<td>87.21</td>
<td>152.2</td>
<td>85.63</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>106.8</td>
<td>85</td>
<td>150.86</td>
<td>83.56</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>105.46</td>
<td>71.83</td>
<td>149.03</td>
<td>68.65</td>
</tr>
<tr>
<td>250</td>
<td>10</td>
<td>104.63</td>
<td>54.58</td>
<td>147.36</td>
<td>43.61</td>
</tr>
<tr>
<td>HLIPP203K1.18-200 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>117.13</td>
<td>96.32</td>
<td>155.03</td>
<td>97.89</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>116.13</td>
<td>100.64</td>
<td>154.53</td>
<td>100.05</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>113.13</td>
<td>82.45</td>
<td>152.53</td>
<td>74.08</td>
</tr>
<tr>
<td>250</td>
<td>10</td>
<td>112.13</td>
<td>62.65</td>
<td>150.86</td>
<td>52.04</td>
</tr>
<tr>
<td>HLIPP276K1.15-375 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>3</td>
<td>122.13</td>
<td>86</td>
<td>154.7</td>
<td>94.11</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>121.46</td>
<td>91.37</td>
<td>154.03</td>
<td>91.88</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>120.13</td>
<td>64.26</td>
<td>150.86</td>
<td>55.3</td>
</tr>
<tr>
<td>250</td>
<td>10</td>
<td>119.13</td>
<td>63</td>
<td>150.86</td>
<td>55</td>
</tr>
</tbody>
</table>

52
By changing the initial fusion conditions, the peak $T_c$ (correlated with crystallization rate) indeed changes due to melt memory effect, but the change is equally apparent in all the three samples of series 1 and diene addition has no influence at all on the observed change. Therefore, the possibility that the existence of melt memory effect or presence of mesomorphic form exclusively in the H-linked samples may be responsible for the wide difference in $T_c$ (table 1) compared to the linear isotactic polypropylene can be ruled out.

The figures (3.7-3.12) and table (3.4) also indicate that there is a big decrease (at least 25-40J/gm) in the heat of fusion ($\Delta H_{\text{melting}}$) and heat of crystallization ($\Delta H_{\text{crystallization}}$) values by increasing the initial melt temperature from 200°C to 250°C for each of the samples. Given that these copolymers are free of additives and melt stabilizers, thermal or oxidative degradation due to high temperature could be a possibility for the observed reduction in heat of fusion. In order to probe this possibility FTIR spectroscopy was performed on three different specimen of IPP150K1.31 each having different initial melt condition. The result is shown in figure 3.13.

The C-CH$_3$ vibration appears at 1380 cm$^{-1}$. The spectra show that this vibration decreased with increasing the initial melt temperature from 200 to 250°C, thus confirming the thermal degradation during the high temperature treatment$^{114}$.

![FTIR spectra](image.png)

**Figure 3.13** FTIR spectra of three different specimen of IPP150K1.31, each having different initial melt condition as indicated in the figure. The peak generated due to C-CH$_3$ bond interaction at 1380 cm$^{-1}$ is shown by an arrow. Note that the intensity of the peak decreases by increasing the initial melt temperature to 250°C from 200°C, indicating scission of the C-CH$_3$ bond.
3.1.2 Isothermal crystallization

3.1.2.1 Crystallization of isotactic poly(propylenes)

It has long been recognized that unlike crystallization of most monomeric substances, polymer crystallization occurs under conditions far removed from equilibrium\textsuperscript{115, 116}. Such behavior is attributed to the long chain nature of the polymeric molecules, which makes it difficult for these chains to disentangle from each other in a disorganized and entangled melt, and subsequently for the chains to achieve a regular conformation and align parallel to each other to form an ordered crystal structure. This is the origin of the semicrystalline nature of polymers, since only a fraction of the polymer chains are transformed into crystals under such conditions of restraint. The two major phases that have been conventionally described in a semicrystalline polymer are the ordered crystalline phase and the disordered amorphous phase. In between these two regions there is an interface connecting the crystalline and amorphous region where the order is dissipated. These phases have distinctly different chain conformations, as represented in figure 3.14. Further introduction of chain irregularities, such as branches, in the backbone reduces the ability of chains to achieve the order required for formation of stable crystals, and suppresses crystallization. Thus, the presence of such irregularities strongly influences the mechanism of crystallization and consequently the nature of crystals formed in the polymers.

![Figure 3.14 Schematic representation of the semicrystalline lamellae. (Reproduced from P.J. Flory, J. Am. Chem. Soc, 1962, 84, 2857)](image-url)
Studies related to the crystallization process of semicrystalline polymers are of great importance in polymer processing, because the resulting physical properties are strongly dependent on the crystallinity and morphology. It is therefore very important to understand the structure-property inter-relationships of the materials to be processed. Namely, in the processing of a semicrystalline polymer, the rheological and crystallization characteristics deeply participate in all the steps of macroscopic shaping and microscopic change of higher order structure.

The crystallization behavior from the melt of isotactic poly(propylenes), prepared with heterogeneous Ziegler-Natta catalysts, has been extensively studied during the last few decades. The study of crystallization behavior and kinetics of iPPs started parallel to its invention, first using dilatometry\textsuperscript{117} and optical microscopy\textsuperscript{118}. It was observed from these studies that the crystallization follows the kinetics of a nucleation controlled process. Since then, many other methods such as light depolarizing microscopy (LDM)\textsuperscript{119}, infrared microscopy\textsuperscript{120} and differential scanning calorimetry\textsuperscript{121} have also been used to follow the development of crystallinity.

Griffith\textsuperscript{122} observed that for an isotactic PP sample the crystallization rate varies inversely with the molecular weight, subsequently Parrini\textsuperscript{123} documented that compared with a polydisperse sample, the narrowly distributed sample has lower crystallization rate. Based on the optical microscopy and X-ray diffraction observations, Hoshino\textsuperscript{124} proposed that the crystallization of isotactic PP consists of two stages: primary and secondary crystallization. However, Martuscelli\textsuperscript{125} and Avella\textsuperscript{126} pointed out that the secondary crystallization occurs only in a lower degree of stereoregularity, which suggests that the secondary crystallization results from the presence of some configurational irregularity (defects) in the chains of iPP. These authors have systematically investigated the influence of the degree of stereoregularity on the overall rate of crystallization of fractions of Ziegler-Natta catalyzed isotactic poly(propylene) and concluded that at constant crystallization temperature the overall rate of crystallization decreases with increase of configurational chain defects.

With the development of a new generation of homogenous transition metal catalysts (metallocene) for the isospecific polymerization of olefins, isotactic poly(propylenes) with a wide variety of microstructures have become available\textsuperscript{127}. The polydispersity decreases and the defect distribution narrows down from chain to chain. As a result, using metallocene catalyzed poly(propylenes) the molecular weight can be varied over a broad range maintaining the same
defect concentrations. With these new iPPs the effect of molecular weight and defect concentration on the crystallization behavior can be studied independently.\textsuperscript{48}

ZN catalyst produces polymers having broad distribution of defect composition, which is in contrast to metallocene catalyst. Cheng et al. observed that in a set of ZN polypropylene fractions with different isotacticity, the linear growth rate decreased by 3 orders of magnitude with a decrease in isotacticity from 0.98 to 0.78 at a constant undercooling. Whereas De Rosa\textsuperscript{128} studying metallocene samples suggested that the crystallization rate increases with increase in concentration of stereodefects and decreasing the molar mass. This unexpected behavior was argued considering that the stereodefects are highly tolerated in the crystalline lattices of $\alpha$ and $\gamma$ forms of i-PP and increase the chain flexibility, which helps the polymer to crystallize faster. However, recently Alamo et. al.\textsuperscript{129} contradicted the conclusion reached by De Rosa on the basis that the stereo defects are partially rejected from the crystals and demonstrated that the crystallization rate decreases with increase in stereo defect concentration.

The parameters that affect the crystallization rate are summarized in the next section.

### 3.1.2.2 Factors influencing crystallization rates

The major factors affecting the crystallization rates are:

- **Undercooling.** As the undercooling ($T_m^0 - T_c$) increases, both the overall and linear growth rate increases.

- **Nucleation density.** As the number of nuclei increases the overall crystallization rate increases.

- **Defect concentration.** (Includes Branching in the polymer chain)
  With decrease in defect concentration both the overall and linear growth rate increase.

- **Molecular weight.** As $M$ increases, increased entanglements or restrictions for the chains to reach the growing crystal, reduced the rate.

- **Polymorphism.** A changeover from $\alpha$ to $\gamma$ polymorph reduces the linear growth rate.
A summary of the effect of LCB and molecular weight on the rate of crystallization is already provided in the introduction of this thesis, few other influencing factors and conclusions from some previous works will be outlined in this section.

According to Turnbull Fisher equation (equation 3.1), the rate of nucleation is controlled by two factors, i.e. transport of molecules to the surface (viscosity effect) and energy needed to form a stable nucleus (thermodynamic effect).

\[ N = N_0 \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{\Delta F^*}{RT}\right) \]  

(3.1)

Where,

- \( N_0 \) = Pre exponential term, involving all the terms weakly dependent on temperature.
- \( E_D \) = Free energy of activation for segmental transport across the liquid crystal interface.
- \( \Delta F^* \) = Free energy change required to form a stable nucleus from the undercooled liquid.
- \( R \) = Gas constant.

This equation allows the observed temperature dependence on crystallization rates to be understood in terms of these two competing (transport and nucleation) processes. At high \( T_c \), the rate of nucleation becomes slow whereas the mobility of the chains is high and the viscosity is low. As a result, the process is governed by nucleation. At low temperature the motion of the chains are restricted because of higher viscosity whereas the rate of nucleation is increased owing to favorable thermodynamic conditions.

The crystalline phase for a highly ordered polymer develops at a reasonable rate only at temperatures well below the equilibrium melting temperature, the state that is actually observed in a real system is a nonequilibrium one. The constitution and properties of the state that is achieved are the result of the competition between the kinetic factors involved in transformation and the requirements for thermodynamic equilibrium. A complete understanding of properties and behavior of crystalline polymeric systems requires knowledge and information of the mechanisms involved in the transformation. In principle, this information can be deduced from crystallization kinetic experiments.

The mass of the material crystallized as a function of time can be estimated from the overall crystallization rate data obtained using DSC. However, the crystallization rate can also be measured by observing a specific morphological feature (spherulite, figure 3.15) using microscopic methods, as detailed in the experimental section. Spherulites are the most commonly
observed supermolecular structure, and are abundantly seen in polymer crystallization but they are not universal. A number of factors like molecular weight, crystallization temperature and chain structure impact spherulite formation\textsuperscript{130, 131}. It is generally observed that the rate of spherulite formation and growth increases with undercooling\textsuperscript{132} (i.e. at lower Tc’s).

**Figure 3.15** Schematic of a typical polymer spherulite (Adapted from, J.D.Hoffman, G.T.Davis and J.I.Lauritzen, 1976, Treatise on Solid State Chemistry, Hanny, N.B., Ed., Plenum Press, New York 3, page 520)

It has already been demonstrated\textsuperscript{52} that for metallocene type polypropylenes the effect of molecular weight on the overall crystallization kinetics is not significant in the range of molecular mass from 68K-288K. This is the range of molar mass studied in this work. The difference between overall defect contents of the linear and H-linked samples (for samples of series the defect content ranges from 1.15mol\% to 1.3mol\%) is also not significant enough to influence the overall rate of crystallization. To make this assertion, we take for example the kinetic data given in reference\textsuperscript{140} for metallocenes with defects changing from 0.3 to 2.3 mol\%. The effect of H-links produced by the addition of diene will be the only relevant parameter that may influence the overall crystallization rates. Addition of H-links may cause a difference in chain entanglement or may behave as an additional effect, both of which can have a significant effect on the overall crystallization kinetics. Thus, focus of this work will be to determine the
exclusive effect of H-links produced by addition of ppm levels of diene on the overall crystallization rate of these “long-branched iPPs” in reference to the linear iPP chain.

The branch points are expected to hinder the polymer chains from packing regularly for the effective crystallization. The effect of short chain branching on the crystallization rate has been studied earlier for both random and uniform ethylene copolymers. For random ethylene 1-hexene copolymers containing butyl branches, Alamo et al. observed that with increase in co-unit content (branching) the crystallization rate decreases drastically. Similarly for metallocene catalyzed uniform ethylene 1-butene copolymers with high butene content (upto 8.5%) and very low polydispersity a dramatic decrease in the crystallization temperature and crystallization rate was observed. The crystallization temperature and crystallization rate were highly branch-content dependent, and in the molecular weight range studied, the effect of molecular weight was less important. The study of crystallization kinetics of short chain branched polyamides (well defined heptyl branches, <3 branches per 1000 atoms in the chain) concluded that the presence of small amount of short chain branches sensibly slows down the overall crystallization kinetics and the spherulitic linear growth rate.

The crystallization kinetics of long, hyper-branched poly(caprolactones) (PCL) were studied by Choi et al. Investigated were PCLs with different number of branch points, characterized as HPCL-5, HPCL-10, HPCL-20, where the digits represent the number of carbon atoms in the linear chain between each branch point. The molecular weight of the linear and hyper-branched PCLs was similar for the samples studied. Crystallization kinetics were inferred from the crystallization peaks observed on cooling the melt at rates ranging from 2 to 10°C/min. The authors observed that when the branches are few and negligible there is an increase in the overall crystallization rate compared to the linear counterpart, which is contrary to the observations and findings in other branched polymeric systems, as mentioned in the previous paragraph. However, with increase in branch density the crystallization rate decreases compared to the linear polymer. In this paper, the nonisothermal crystallization exotherms of the HPCL’s and LPCL were measured by DSC at various cooling rates ranging from 2 to 10 °C/min. During the controlled cooling from the melt, the HPCLs with longer linear segments and fewer branches experienced faster crystallization.

The slower crystallization rate of LPCL compared to that of the HPCL-20 was an unexpected behavior because LPCL consisted of only one long chain with no chain
heterogeneity. Steady shear melt viscosity measurements performed at various temperatures interpreted that the cooperative chain mobility of the HPCL-20 is higher than that of LPCL in their melt state, indicating a faster diffusion of polymer chains to crystallize. In addition, the linear segments incorporated in the HPCL-20 are relatively long such that the thermodynamic condition for crystallization of ordered chains in parallel array could be nearly equivalent to that of LPCL, causing the overall crystallization of the HPCL-20 to occur at a faster rate than LPCL.

In an additional paper an analysis of the effect of branches on the crystallization kinetics of PET\textsuperscript{72} led to the conclusion that the presence of branching and linear disruptions, in small concentrations, appear to enhance the crystallization process. It was postulated that possibly, a small number of branches act as to facilitate nucleation. At higher concentrations of such defects, however, the crystallization process is slowed down and the overall crystallinity of the PET is reduced.

A molecular dynamic analysis of the crystallization process that may occur in LLDPE has been performed\textsuperscript{136} indicating that there are two ways in which a branch affects the crystallization process. One is that in the nucleation the branches act as sites for further nucleation and another is that in the crystal growth the branch is rejected from the crystal region as defect. However, in a recent paper the MD result obtained by Zhang et .al.\textsuperscript{137} was proven to be incorrect by Alamo et.al.\textsuperscript{138}, as they evidenced that the small side groups, i.e. halogens, are also fully incorporated in the crystalline regions of precisely substituted PE’s.

Taking these works as reference, we could postulate that if the iPP long branches act as nucleating seeds in the crystallization process, one would expect LCB iPPs to exhibit higher nucleation density than the linear polymer. This nucleation density increase will result into faster overall crystallization rates compared to the linear polypropylene sample.

Another important way to study crystallization kinetics is by measuring the rate of formation and growth of spherulitic structure. The growth rate of spherulites is both a diffusion and nucleation controlled process. The nucleation rate decreases with increasing temperature whereas the diffusion rate increases with temperature. These two competing factors are responsible for the observance of a maximum in the growth rate with temperature. The rate at which a lamellar crystal grows (that is, the rate of advance of a crystal normal to its surface) can be observed directly by optical microscopy.
The strong effect of concentration of defects in lowering the growth rates for metallocene iPPs of a fixed molar mass was earlier reported\textsuperscript{139} and the variation of growth rate with defect was quantified. It was observed that the growth rate decreased about two orders of magnitude with increasing the defect content from 0.3-2.35 mol\%. The defects in polypropylene molecules act as non-crystallizable units. An increase in non-crystallizable structural irregularity leads to a reduction in the amount of crystallizable sequences and, thus, to a decrease in the rate of crystallization\textsuperscript{139}. Also a small but systematic decrease of rate with molar mass was observed for metallocene catalyzed isotactic PP fractions in a range of molar mass from 86,000 to 383,000\textsuperscript{139}. The variation of rate with molar mass is attributed to the increased number of entanglements per chain in the melt, which affects segmental transport in the crystallization process. The relation between the spherulite growth rate, molecular weight and crystallization temperature follows a similar general pattern. It was pointed out previously that both overall crystallization rate and the crystallinity level that can be attained decrease with molecular weight as a consequence of chain entanglements in the melt. Further investigations have shown that the spherulite growth rates and primary nucleation rate also depend on the entanglement density\textsuperscript{140}. The spherulite growth rate is increased by 25-45\% for a partially disentangled melt relative to a melt with a normal concentration of entanglements\textsuperscript{141}. The melt was disentangled by keeping the samples for a sufficiently longer time above their melting temperature\textsuperscript{141}.

An empirical relation has been proposed by Cheng and Wunderlich\textsuperscript{142} to explain the variation of the growth rate with molecular weight. This relation can be expressed as,

$$\log G = A \log (\ln M) + B$$ \hspace{1cm} (3.2)

The constants $A$ and $B$ depend on the crystallization temperature, or undercooling. In this expression with $A$ negative, $G$ monotonically decreases as a function of $M$. Later on, Deslandes et al. studied the molecular weight - growth rate relation for poly(aryl ether ether ketone)\textsuperscript{143}, and the following empirical relation was proposed,

$$\log G(T_c) = \log A(T_c) + B(T_c) \log M_n$$ \hspace{1cm} (3.3)

where $A(T_c)$ and $B(T_c)$ are both functions of the temperature of crystallization $T_c$. A relationship between $\log G(T_c)$ and $\log M_w$ similar to equation 2 was also given by Lopez and Wilkes\textsuperscript{144} for poly(p-phenylene sulphide). Furthermore, more complex dependences have also been proposed. Magill\textsuperscript{145} arrived empirically at the following equation for poly(tetramethyl-p-silphenylene siloxane),
In \( G(T_c) = \text{const.} + B Mn^{-\alpha} \) (3.4)

It has been generally observed that linear growth rates of semicrystalline polymers can increase, decrease or remain constant with chain length, depending on the molecular weight range of interest and the crystallization temperature analyzed. The interval where those changes occur is specific to a given polymer. As a result although a qualitative description can be offered to the experimental results, quantitative explanation is lacking.

In addition to lowering the growth rate, defects (or comonomers) also induce a different polymorphic form (gamma form) in metallocene iPP’s (see chapter 1 for references on polymorphism in iPP). The influence of the ethylene content (comonomer) on the crystallization kinetics of random propylene ethylene copolymers was evaluated independently from the effects inferred by molecular weight or the presence of different concentrations of stereo or regio defects in our recent paper\(^{47}\). In this work the linear growth rates of a series of metallocene catalyzed novel propylene ethylene copolymers with a content of ethylene ranging from 0.8 to 7.5 mol% were studied. The formation of both the polymorphs \((\alpha+\gamma)\) during isothermal crystallization was evidenced by WAXS.

The crystallization behavior of pure gamma phase was isolated from the crystallization of mixed \((\alpha+\gamma)\) phases in our previous paper on ethylene-propylene copolymer\(^{47}\). The crystallization of pure \(\gamma\) crystallites can be monitored by extending the measurements of the spherulitic radius with time to the region where pure gamma form prevails. This is not experimentally feasible at the lowest isothermal \(T_c\)’s because the spherulites impinge before the content of alpha phase levels off. At higher \(T_c\)’s the nucleation density decreases and the spherulitic growth can be followed up to the region of pure or predominantly \(\gamma\) growth before impingement. A sharp break between two growth domains at temperatures and time frames that correlate to the simultaneous growth of mixed \(\alpha\) and \(\gamma\) polymorphs at the early stages and with the growth of pure gamma crystallites at a later stage in the transformation is observed. As a result it can be concluded that the crystallization of pure gamma phase proceeds with significantly lower linear growth rates than those corresponding to the formation and growth of mixed polymorphic forms. As suggested by Meile\(^{146}\), the existence of non parallel chain orientations in gamma polymorph poses a possible limitation on the growth mechanism of this polymorph and makes it kinetically disfavored.
To summarize, it can be stated that in the present study, for a set of metallocene catalyzed H-linked iPP crystallized at a fixed temperature, the difference in molecular weight, defect concentration, polymorphic content and the effect of H-linkages on the nucleation activity will be the major parameters influencing the crystallization rates compared to its linear counterpart. From the molecular characterization of the two series of samples (experimental section) one can easily rule out the influence of defect content on the crystallization kinetics as the difference is minimal. The moderate difference between molecular weights may not also be the determining factor to account for any observed difference in the rate of crystallization. Thus, the most relevant parameter to consider while analyzing the crystallization kinetics and comparing the overall or linear growth rate between the linear and H-linked iPP’s will be the effect of H-links or diene addition on the linear chain.

3.1.2.3 Analysis of overall crystallization rate using nucleation theory

The overall crystallization process is controlled by primary nucleation and growth. Primary nucleation is the process by which segments of molten polymer chains become aligned to form nuclei when the polymer melt is cooled down below its equilibrium melting temperature. Growth of the polymer crystals occurs by a process of secondary nucleation on a pre-existing crystal surface. The first step in the secondary nucleation process is the laying down of a molecular strand on an otherwise smooth crystal surface. This is followed by subsequent addition of further segments through chain folding process. Chain folding occurs for flexible polymer molecules whereas extended chain crystals are obtained for rigid ones.

Nucleation theory has been important in analyzing and understanding the kinetics of isothermal crystallization from the melt and the temperature coefficient of this process. In this theory the dependence of nucleation rate \( N \) on the crystallization temperature, \( T \) is described by equation 3.1\(^{147}\).

DSC, WAXD and SAXS are used to determine the crystallization rates \( (t_{1/2}) \), of linear and LCB (H-linked) samples (those termed “series 1” of our work) from sheared melts by Agarwal et. al\(^ {37}\). This work also studied the flow induced crystallization behavior of propylene diene copolymers in reference to the linear chain and observed that the crystallization kinetics of the LCB samples increased by at least one order of magnitude relative to the linear resin. Under shear there is an effect of orientation on the melt and the increase in the rate of crystallization is
attributed to an increase in the crystal nuclei, due to this orientation of the polymer molecules. A stable crystallization precursor structure in the sheared melt is formed.

By crystallizing from quiescent melts, the effect of LCB formed by addition of diene on the crystallization rate of linear iPP can be studied independently without the influence of shear. Shear induces orientation and that affects the crystallization kinetics, therefore the present study from quiescent melt would allow us to probe whether it is the difference in entropy of isotropic melt that led to such unusual behavior of enhancement in crystallization rates with increase in branching.

The results of heating and cooling of the two series of samples at 10°C/min in section 3.1.1 indicate faster rates with increase in diene, an open question is, if the increase in rates is due to molecular weight or due to the presence of LCB. To probe this, the effect of H-links exclusively (keeping mol wt. fixed) on the overall crystallization rates can be investigated by carrying out isothermal and non-isothermal crystallization of the samples of series 2.

The overall crystallization rates from quiescent melts of linear and H-branched iPPs of both series were measured by DSC, and taken as the inverse of time taken to reach the peak of the exotherm \( t_{1/2} \), as detailed in the experimental part. The rate is plotted in Figure 3.16 against crystallization temperature for the first series.

Different features are apparent from this plot. The large negative temperature coefficient of the crystallization rate that is observed in the figure is a general feature of polymer crystallization indicating nucleation-controlled process\(^7\). From the figure it is observed that the rate of crystallization is directly proportional to the amount of diene incorporated, i.e. the linear sample has the lowest overall crystallization rate and the increase in rate parallels the diene content. Quantitatively, at \( T_c = 130°C \) it takes 52.7 minutes for the linear to acquire half of the transformation, for sample with 200ppm diene it takes 6.7 minutes and for sample with 375ppm of diene it takes 1.9 minutes. Then, we see that compared to the linear sample, 200 ppm of diene decreases by 8 fold the time for half of the crystallization and by 28 fold for the sample with 375 ppm diene. The overall rate of crystallization of both diene containing samples are significantly higher than the linear one by at least an order of magnitude, the same difference is observed in the entire range of crystallization temperature \( (T_c) \) studied.

This behavior is in accordance with the optical micrographs comparing nucleation density (shown in section 3.1.1.2). From the representative images of the linear and H-linked
samples at 130°C it can be concluded that the nucleation densities of H-linked samples are substantially higher than the linear one.

Figure 3.16 Overall crystallization rates of samples of Series 1. The content of diene in ppm is indicated.

Figure 3.17 Overall crystallization rates of samples of Series 2. The content of diene in ppm is indicated.
The crystallization of iPPs of series 2 follows a quite different behavior, as shown in fig 3.17. Although the trend of the overall crystallization rate for the samples of series 2 follows that of series 1, i.e. with increase in diene the rate increases, this effect is not as distinct as it is for series 1. For samples of series 2 there is almost no difference in rates between samples with 100 and 200ppm diene. This may be attributed to the non-uniform distribution of diene in the polypropylene chain.

![Graph](image.png)

**Figure 3.18** Overall crystallization rates for linear and 200ppm diene samples of both series. Samples series 1 are indicated by black points whereas the red ones indicate those of series 2

To emphasize the role of intermolecular distribution of diene on the overall crystallization kinetics, the crystallization rate of the linear iPP and one with 200 ppm of diene is compared in fig 3.18. Quantitatively, one order of magnitude increase in the overall crystallization rate was observed with addition of 200 ppm diene to the linear sample of series 1, i.e. at $T_c = 130^\circ$C it takes 52.7 minutes for the linear to acquire half of the transformation, whereas for sample with 200ppm diene it takes 6.7 minutes However, an increase of only two
fold was obtained for the same quantity (200ppm) of diene addition to the linear sample of series 2, i.e. at Tc = 130°C the linear sample takes 49 minutes to reach half of transformation, whereas the sample with 200ppm diene takes 30 minutes to reach the same. As indicated in the experimental part, the main difference between the two series is the distribution of diene. In series 1 the diene is distributed uniformly in the polymer matrix, whereas in series 2 the diene molecules are targeted to the lower molecular weight chains. Comparing the overall crystallization data it seems that longer molecules with higher contents of LCB in series 1 may be responsible for the observed difference.

The results obtained from the overall crystallization study followed the expectation, as from section 3.1.1.2 it was evident that the nucleation density of the H-linked samples was higher than their linear counterpart, and, this ultimately was responsible for the observed difference in rate. In order to test the nucleating activity conferred by the addition of H-linkages, crystallization rates of externally nucleated samples of series 1, each containing 0.25 % of Millad 3988(3,4-dimethyl dibenzylidene sorbitol) was used as the nucleating agent\textsuperscript{148}, were compared with their non nucleated counterpart. The overall crystallization rate for each pair of the nucleated and non nucleated samples of the series 1 is plotted against temperature in figure 3.19, nucleated samples are characterized by open symbols.

According to the expectation, it is observed that the overall crystallization rates of the nucleated samples are always higher than the non-nucleated ones. The difference in the overall crystallization rates between nucleated and non-nucleated samples narrowed down for the sample with highest diene content (375ppm).

Quantitatively, at Tc = 130°C it takes 52.7 minutes for the linear to acquire half of the transformation, whereas it takes half the time, 25 minutes, for its nucleated counterpart to acquire the half transformation. Similar results are obtained for the sample with 200ppm diene, it takes 6.7 minutes for the non nucleated one to reach half the transformation and its nucleated counterpart takes 3.1 minutes to reach the same. However, this difference is not the same between the sample with 375ppm of diene and its nucleated counterpart, as with nucleation the time taken to reach half the transformation changes from 1.9 to 1.5 minutes for the sample with 375ppm of diene.

From the results of figure 3.19 it can be concluded that the addition of a nucleant to the H-linked iPP with the highest content of diene does not enhance the crystallization rate any
further. Hence, it appears that 375 ppm of diene basically saturates the nucleation activity for iPP.

Figure 3.19 Overall crystallization rates of nucleated and non-nucleated samples of series 1, the open symbols with a N in parenthesis represents data for the nucleated sample. The symbols are matched for non nucleated and their nucleated counterparts.

3.1.2.4 Analysis of overall crystallization rate using Avrami theory

Agarwal et. al.\textsuperscript{37} analyzed the crystallization kinetic data from sheared melt using Avrami theory for the long chain branched (H-linked) samples of series 1. The results are presented in figure 3.20. The analysis of crystallization kinetics using Avrami model indicated a spherulitic crystal geometry for the linear sample which transforms to disklike ones and finally becomes rodlike with increase in LCB (i.e. Avrami exponent falls from 3-1.8 with increase in amount of LCB). The shear treatment enhances the nucleation density of the branched samples compared to the linear one thus forcing a changeover of the crystal geometry from spherulitic to disk and rodlike. The change is interpreted on the basis of Avrami exponents. An exponent of 3 indicates heterogeneous nucleation with formation of 3 dimensional crystallite, i.e. spherulite, whereas an exponent of 2 indicates heterogeneous nucleation with formation of 2 dimensional disklike
crystallite, and an exponent of 1 corresponds to heterogeneous nucleation with 1 dimensional rodlike crystallite.

Figure 3.20 Avrami plot of the crystallization data from sheared melt. The chosen shear mode was a step-shear: shear rate of 60 s⁻¹ and strain of 1430%. This corresponds to a shear duration of $t_s = 0.25$ s. The LCB samples in this figure are same as that of the three samples of series 1 in the present study. LCB corresponds to the linear sample, 05 corresponds to the sample with 200pm diene), and 07 corresponds to the one with 375ppm diene. (Agarwal, et al. *Macromolecules*, 2003, 36, 5226)

The isothermal crystallization kinetics was analyzed from the quiescent melts of two series of H-linked novel propylene diene copolymers. Avrami analysis was performed on the overall crystallization kinetics data in order to study the effect of LCB and molecular weight on the nucleation and growth geometry, the results were compared to those obtained under shear to determine the influence of crystallization conditions on the final result.

It is known that crystallization of polymers is mainly controlled by nucleation and growth mechanisms. Thermodynamic, physical, mechanical and most of the other properties of semicrystalline polymers depend on the structure and morphology that evolves from the melt. As a result in order to understand properties it is very essential to have a clear understanding of the
crystallization mechanism. Studies of crystallization kinetics can often lead to an understanding of the mechanism.

Johnson, Mehl and Avrami analyzed the isothermal crystallization kinetics and Turnbull and Fisher derived the temperature coefficient in condensed systems. Considerable attention has been focused on the crystallization kinetics of isotactic polypropylene (iPP) because of its importance in processing and end use properties. In 1959 Marker, Griffith and Falkai et. al. examined the crystallization behaviour of iPP at different temperatures using dilatometry and optical microscopy methods. They observed that the crystallization follows the kinetics of a nucleation controlled process according to the Avrami equation and the corresponding Avrami exponent is 3. Since then many experimental methods such as light depolarizing microscopy, infrared microscopy and differential scanning calorimeter have also been used in this field of research. Hoshino et. al. also used dilatometry to determine the Avrami exponents of PP and obtained values between 3 and 4. For the isothermal crystallization of PP, the average Avrami exponent has been reported to be 3 by several investigators and it would imply that the crystallization mechanism of PP was composed of instantaneous nucleation and spherulitic growth.

Hoshino et. al. proposed that the crystallization of iPP consists of two stages; primary and secondary crystallization. Avrami equation can be applied to both the stages and the exponent (n) of the former is larger than the latter. Other Modified Avrami models have been formulated in the past to take into account lamellar branching, isothermal thickening during the secondary crystallization.

Hillier proposed the two stage model and analyzed the crystallization kinetics by assuming that the second stage developed following elementary first order kinetics but later acknowledged this to be oversimplification. Price also presented a kinetic theory that considered both primary and secondary crystallization processes during the crystallization of bulk polymers.

Recent studies of the crystallization behavior of poly(propylenes) synthesized with a metallocene catalyst, have evidenced the formation of two polymorphs, monoclinic (α) and orthorhombic (γ) phases. The formation of the γ phase is favored in polypropylenes with chain microstructures characterized by short continuous isotactic sequences (i.e. chains with defect promotes the formation of γ phase). It has been pointed out that the polymorphic
phase with higher stability also possesses a faster rate of formation\textsuperscript{169}. As a result, studies on crystallization kinetics can help us understand the metastability of $\alpha$ and $\gamma$ crystals from the viewpoint of kinetics. Recently, Alamo et. al\textsuperscript{170} demonstrated that the crystallization kinetics of metallocene based propylene copolymers can be analyzed taking into account the simultaneous development of two polymorphic phases ($\alpha$ and $\gamma$) by applying the two stage model on the experimental overall crystallization data.

In the present study the copolymers are metallocene based, therefore, they are expected to exhibit polymorphism, i.e. presence of gamma form in addition to alpha. The amount of gamma form will depend on chain defects and crystallization temperature. It will also be interesting to note whether the presence of gamma form makes the experimental data to be fitted better to a two stage modified Avrami model compared to the single stage and leads to more justified values of Avrami exponents.

Isothermal crystallization followed by melting at 10°C/min was studied for all the samples in both series. The crystallization peaks (exotherms) for the samples of series 1 and series 2 at different isothermal crystallization temperatures ($T_c$) are plotted in figure 3.21 and 3.22 respectively. It is observed that with increase in $T_c$ the time required to reach the peak of the crystallization exotherm (i.e. 50% transformation) increases proportionally. The inverse of the time taken to reach the peak crystallization ($t_{1/2}$) is taken as a measure of the overall crystallization rate. Therefore, the figures indicate that the overall crystallization rate decreases with the increase in $T_c$. The time at which isothermal crystallization begins was taken at the point where the melt is equilibrated at that $T_c$. This point is taken as crystallization time, $t = 0$, and for each $T_c$ the point is illustrated with primary heat flow data in the inset of each figure.

Equation 3.1 implies that the overall crystallization process is governed by two competing mechanism, i.e. the thermodynamic driving force and segmental transport. The present study is carried out in a range of $T_c$ where the thermodynamic term dominates, i.e. the undercooling ($T_m^0 - T_c$) is low. Therefore, the rate of nucleation is very slow whereas the mobility of the chains is high, the process in this temperature range is nucleation controlled and that explains the negative temperature coefficient of the rate.
Figure 3.21 Exotherms of the three samples of Series 1 at indicated Tc’s. The inset illustrates the starting point for crystallization at each Tc, time t = 0
**Figure 3.21** – continued

![Graph](image)

**Figure 3.21** Exotherms of the three samples of Series 1 at indicated Tc’s. The inset illustrates the starting point for crystallization at each Tc, time t = 0

![Graph](image)

**Figure 3.22** Exotherms of the four samples of Series 2 at indicated Tc’s. The inset illustrates the starting point for crystallization at each Tc (a) 0ppm, (b) 50ppm, (c) 100ppm, and (d) 200ppm
Figure 3.22 Exotherms of the four samples of Series 2 at indicated Tc’s. The inset illustrates the starting point for crystallization at each Tc (a) 0ppm, (b) 50ppm, (c) 100ppm, and (d) 200ppm
Subsequent meltings of the isothermally crystallized samples at 10°C/min are plotted in figure 3.23 and 3.24 for series 1 and 2 respectively. Most of the endotherms plotted in the two figures exhibit two melting peaks, the presence of two peaks has been studied well and explained before\textsuperscript{171} as peaks corresponding to two different polymorphic phases are present in the same sample.

\textbf{Figure 3.23} Endotherms of the samples of series 1 at indicated Tc’s (a) 0ppm, (b) 200ppm and (c) 375ppm
The low temperature peak corresponds to the melting of $\gamma$ crystallites and the high temperature one relates with the melting of the crystals in the $\alpha$ phase. The fraction of each polymorph is obtained by deconvolution of the respective peaks and taking their relative ratios. From the endotherms it is also evident that with the increase in isothermal crystallization temperature (Tc) the melting peaks shifts to higher temperatures, this observation was initially explained by Weeks\textsuperscript{172} as a consequence of the increase in lamellar thickness. Following Weeks, later on Alamo et. al.\textsuperscript{173} also interpreted that the higher Tm values at high Tc results from a large increase in the size of the crystals relative to the initial nucleus size.

Figure 3.24 Endotherms of the samples of series 2 at indicated Tc’s, (a) 0ppm, (b)50ppm, (c) 100ppm, and (d) 200ppm
Figure 3.24 – continued

The exothermic peak is associated with the development of crystallinity. This peak is integrated to calculate the degree of crystallinity developing as a function of time. The isothermal phase transition of polymer crystallization can be described by the Avrami equation in order to study the isothermal crystallization kinetics of polymers. According to Johnson, Mehl
and Avrami the change of crystalline fraction \( x \) with time \( t \) in isothermal crystallization is expressed by the following equation:

\[
1 - x = \exp(-X_{\text{ext}})
\]  

(3.5)

\( X_{\text{ext}} \) is the integral over the transformation time (\( t \)) of the volume (\( v \)) of any growing center, with birth at time \( \tau \), times the total number of nuclei that could be generated in the total volume.

\[
X_{\text{ext}} = \int_0^t v(t, \tau) I(\tau) d\tau
\]

(3.6)

I(\( \tau \)) = number of nuclei generated per unit volume and per unit time.

The most general form of the Avrami equation results from combining the above two equations

\[
X(t) = \left[ 1 - \exp\left( -\int_0^t v(t, \tau) I(\tau) d\tau \right) \right]
\]

(3.7)

\( X_{\text{ext}} \) can be written as, \( X_{\text{ext}} = kt^n \), \( n \) is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, and \( k \) is a crystallization kinetic constant.

Thus, equation (3.5) can be written as, \( 1 - x = \exp(-kt^n) \)    

(3.8)

The \( n \) values for specific geometries corresponding to heterogenous and homogenous are given in table 3.5. In heterogeneous nucleation we consider that a fixed number of nuclei per unit volume, \( N \), pre-exists in the melt. These nuclei further grow to form crystals. In homogenous nucleation, the nuclei appears with a constant nucleation rate and subsequently grows to form crystals.

<table>
<thead>
<tr>
<th>Growth geometry</th>
<th>Homogenous nucleation</th>
<th>Heterogeneous nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 dimensional, spherulitic</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2 dimensional, disklike</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>1 dimensional, rodlike</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.5 Values of exponent \( n \) for various types of nucleation and growth acts (assuming linear growth)  
The mass fraction of crystalline material, $x$, at time, $t$, can be calculated from the ratio of the area under the DSC curve from $t = 0$ to $t = t$, and the total area under the isothermal curve. The mass fraction of crystallinity as a function of time for the two series of isotactic polypropylene resins is shown in fig 3.25 and 3.26. In the figures there is an initial time where crystallinity is not detected. This is followed by an accelerated rate of development of transformed material. Finally there is a leveling off in the crystallization rate as a certain degree of crystallinity is approached. The data are analyzed according to classical one stage Avrami kinetics given by equation 8. The experimental curves for each of the samples in figure 3.25 and 3.26 have been obtained from the crystallization exotherms of figure 3.21 and 3.22 respectively.

**Figure 3.25** Development of crystallinity as a function of time for samples of series 1. The dotted lines indicate a fitting of the experimental results with theoretical models of $n=3$ and $4$, the crystallization temperatures are indicated for each curve, (a)IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15
Figure 3.25 – continued

Figure 3.25 Development of crystallinity as a function of time for samples of series 1. The dotted lines indicate a fitting of the experimental results with theoretical models of n=3 and 4, the crystallization temperatures are indicated for each curve, (a)IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15

Impingement of the spherulites reduces the total material available for crystallization thus decreases the rate of crystallization causing the leveling off in the plot. The plot becomes linear for the mid period of the crystallization. Four different temperatures are shown for each of the samples, the temperature interval was chosen between 120-136°C, which corresponds to the temperature range where the samples exhibit maximum gamma content. In the temperature range studied both polymorphs were also observed at the earliest detection of crystallinity. The $\alpha$ phase likely acts as effective seeds to nucleate and grow gamma branching, once a $\alpha$ surface is generated, a subsequent epitaxial growth of $\gamma$ crystals from this surface follows\textsuperscript{174}. The optical microscopy study of the samples used in present work indicated that the nucleation event appeared to be instantaneous for all of the polymers, and, all of them developed well defined spherulitic morphology except the two diene containing samples in series 1. These two did not form well defined spherulites owing to their extremely high nucleation densities in the temperature range studied. The study is detailed in morphology section.
Figure 3.26 Development of crystallinity as a function of time for samples of series 2. The dotted lines indicate a fitting of the experimental results with theoretical models of $n=3$ and $4$, the crystallization temperatures are indicated for each curve, (a) IPP291K1, (b) HLIPP275K1, (c) HLIPP283K1 and (d) HLIPP247K1
The linear form of equation 3.8 can be written as,

$$\ln[-\ln(1-x)] = \ln k + n \ln t$$  \hspace{1cm} (3.9)

The experimental data according to equation 3.9 for the samples of series 1 and 2 are plotted in figure 3.27 and 3.28 respectively. In these figures theoretical lines for n=3 (heterogenous nucleation with three dimensional growth) and n=4 (homogeneous nucleation with three dimensional growth) are shown and the slopes are compared with the experimental data. From the figures, it is evident that the line with slope 3 (n=3) is parallel to the experimental data for the linear sample of series1 at Tc = 127 and 128°C. For diene containing samples and the linear sample for series 2 the experimental data yield a non-linear behavior in these plots, even at low transformation levels, and deviate strongly from theoretical models at all temperatures studied.
Figure 3.27 Plots of $-\ln(1-X_c)$ vs ln t for samples of series 1. Tc’s are indicates for each curve, (a) IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15
The linear form of the equation (3.8) is appropriate mainly for the low levels of transformation. The theoretical lines and experimental plots are compared for the samples of series 1 and 2 in fig 3.25 and 3.26 respectively. Four different temperatures are plotted for each of the samples. For linear sample at Tc = 126 and 130°C n=3 seems to fit well at the initial levels of transformation but then it deviates slightly in the intermediate levels of transformation and again matches well at the higher level of transformation. For the diene containing samples in series 1, n=3 does not fit well either in initial or higher levels of transformation. The n=4 plot follows well for the experimental data of the diene containing samples especially at lower temperatures and till about 25-35% levels of transformations. The fit becomes poorer with increase in temperature.

The addition of diene considerably increases the nucleation density of the H-linked samples to a compared to the linear one. Piorkowska\textsuperscript{175} observed that the increase in nucleation density caused by fibre addition in polymer matrices makes the crystallization kinetics of the system inappropriate to be described by classical one-stage Avrami equation as the plots were non linear in nature (i.e. not conforming to an integer value of n, Avrami exponent). Therefore, in the present study the increase in nucleation density may be one of the reasons for the deviation of these H-linked samples from the classical one stage Avrami model.

The linear sample in series 2 does not follow the same behaviour as observed for the linear sample in series 1, i.e. the experimental data does not fit n = 3 except only at 130°C. Experimental data at 128°C (figure 3.28) could not be fitted to theoretical Avrami relations with either n = 3 or n = 4 at any levels of transformation. However, at 124 and 126°C, the experimental data fits to the initial levels of transformation with theoretical model of n = 4. For the sample with lowest diene content (HLIPP275K1, 50ppm) the experimental data could not be fitted with theoretical model of either n=3 nor n= at all the temperatures (Tc) studied. The samples with higher diene content (100 and 200 ppm) in series 2 follow similar behavior exhibited by the diene containing samples of series 1, i.e. the experimental data, especially at initial levels of transformations (till 30-40%) can be fitted well to the theoretical model corresponding to n=4.

Hence, it appears that the experimental kinetics follow a combined physical model. The model for n =3 appears to represent to a greater extent the kinetics of the linear sample in series
1, whereas experimental data of crystallizations in diene containing samples, at least in the initial levels of transformations, fits better to the theoretical model with $n=4$. However, some experimental data could not be fitted to the theoretical model at any level of transformations.

**Figure 3.28** Plots of $[-\ln(1-X_c) \text{ vs } \ln t]$ for samples of series 2. $T_c$’s are indicated for each curve, (a) IPP291K1, (b) HLIPP275K1, (c) HLIPP283K1 and (d) HLIPP247K1
Figure 3.28 – continued

Figure 3.28 Plots of \([-\ln(1-Xc) \text{ vs } \ln t]\) for samples of series 2. Tc’s are indicates for each curve, (a) IPP291K1, (b) HLIPP275K1, (c) HLIPP283K1 and (d) HLIPP247K1

The non-linear behaviour of the experimental data (fig 3.27 and 3.28) and poor fit with the theoretical models (fig 3.25 and 3.26) indicates the requirement of a two stage model that may also account, and provide some justification, for the simultaneous development of the \(\alpha\) and \(\gamma\) polymorphic forms in the samples studied at the specified temperature range.
A modified Avrami model consisting of parallel two stage (primary and secondary) kinetics was first considered by Hillier\textsuperscript{164}. According to this model, during the first step, spherulites nucleate and grow isotropically from 0-t, up to crystallinity $X_p\propto$. A second step occurs within primary process in a time frame $\tau$-t, with same basic kinetics, but the nucleation and growth laws might be different. Some low molecular weight polymers that were ejected and trapped in interfibrillar layers during first step, crystallize in the second step leading to an Avrami exponent approximately equal to unity.

The variation of crystallinity from each stage is given by:-

Primary

$$X_{p(t)} = X_{p}^{\infty} \left[ 1 - \exp \left( - k_p t^n \right) \right]$$  \hspace{1cm} (3.10)

Secondary

$$X_{s(t-\tau)} = X_{s}^{\infty} \left[ 1 - \exp \left( - k_s (t - \tau)^n \right) \right]$$  \hspace{1cm} (3.11)

The crystallinity at time t, developed from the two processes is given as-

$$X_c(t) = X_{p(t)} - \int_{0}^{t} \frac{d}{d\tau} \left[ X_{s(t-\tau)} \right] d\tau$$  \hspace{1cm} (3.12)

In this equation the integral term accounts for the correlation between the two stages.

Optical microscopy studies revealed that the nucleation of these iPPs is instantaneous and spherulites grow linearly with time. Based on these features, the Avrami kinetics associated with this process should give $n = 3$ for the development of $\alpha$ phase. Either the gamma phase nucleates within the alpha crystals from initial levels of transformation or they develop and grow as individual gamma crystals. If they develop within the parent alpha phase then the nucleation of the $\gamma$ phase is considered to proceed at a constant rate because it depends on the presence and constant linear growth of $\alpha$ crystals. That would ideally lead the kinetics of gamma growth to have a value of $m = 4$. However, gamma crystals grow within the parent alpha crystal, therefore its growth is restricted to the volume of the $\alpha$ phase forming. Considering this, the expected Avrami exponents for the $\gamma$ stage will be either $m = 3$ (two dimensional growth) or $m = 2$ (one dimensional growth or lamellar growth restricted in two dimensions). Should gamma crystal grow unrestricted as individual spherulites from the isotropic melt, then the kinetics would be similar to that of homogeneous nucleation (nucleation occurs at constant rate throughout the
transformation), with exponent of m=4. The latter is more probable at Tcs where the content of gamma is much higher than that of alpha.

Substituting equation 3.10 and 3.11 into equation 3.12 and normalizing with respect to the total crystallinity \(X_c\), we get

\[
X(t) = \frac{X_{(t)}}{X_c} = \frac{X_{\alpha}^\infty}{X_c} \left[1 - \exp(-k_\alpha t^n)\right] + \frac{X_{\gamma}^\infty}{X_c} \int_0^t (t - \tau)^{m-1} \left[1 - \exp(-k_\gamma \tau^n)\right] \exp\left(-k_\gamma (t - \tau)^m\right) d\tau
\]

(3.13)

where \(\frac{X_{\alpha}^\infty}{X_c}\) and \(\frac{X_{\gamma}^\infty}{X_c}\) are the fractions of crystals developed from the first and second stage respectively out of the total crystals formed (\(X_{\alpha}^\infty + X_{\gamma}^\infty = X_c^\infty\)).

Substituting, \(\frac{X_{\alpha}^\infty}{X_c} = w_\alpha\) and \(\frac{X_{\gamma}^\infty}{X_c} = (1 - w_\alpha)\), in equation 3.9, where \(w_\alpha\) and \((1 - w_\alpha)\) are the fractions of \(\alpha\) and \(\gamma\) crystals at the end of the transformation, we get

\[
X(t) = w_\alpha \left[1 - \exp(-k_\alpha t^n)\right] + (1 - w_\alpha)k_\alpha \int_0^t (t - \tau)^{m-1} \left[1 - \exp(-k_\gamma \tau^n)\right] \exp\left(-k_\gamma (t - \tau)^m\right) d\tau
\]

(3.14)

As in a previous work\(^\text{170}\) equation (3.14) was evaluated using numerical quadrature in Matlab. For each experimental data set, the values of m and n were varied systematically in the range 1.5 to 4.5, in increments of 0.1 and values of \(K_\alpha\) and \(K_\gamma\) that minimized the sum of the square of the deviations (SSD) were determined using MATLAB. Values of \(w_\alpha\) at each \(T_c\) were obtained from the heat of fusion values. The nonlinear regression was carried out with starting guess values for the rate constants \((K_\alpha\) and \(K_\gamma))\) that were estimated from the initial slopes of the single stage linearized Avrami plots.

With increase in transformation level the transformation rate decreases owing to formation of entanglements and knots within the polymer chain and forces the experimental data of figures 3.25 and 3.26 to deviate from the theoretical model. Therefore, fits of the experimental model were restricted to transformation levels of 60%. Experimental (continuous lines) and best results from the non-linear regression fits (dotted lines) for the fractions of transformed material with time are shown in figure 3.29 and 3.30 for the samples of series 1 and 2 respectively for four representative Tc’s for each polymer. It is evident that the two-stage model allows fits of the experimental data to relatively high degrees of transformation, thus justifying the choice of
applying two stage model in correlation with the development of two different polymorphic forms simultaneously. The two stage model thus overcomes the limitation of the classical one stage Avrami model.

Figure 3.29 2-Stage Hillier model fits for samples of series 1 (Solid line represents experimental data and dashed line represents the fit with equation 3.14) (a) IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15
Figure 3.29 – continued

The linear sample of series 1 followed n=3 (in single stage model) till 80-90% (at Tc=127 and 128°C) of transformation, which verifies that alpha crystals nucleate heterogeneously and form spherulitic structures, this fact was also established earlier by optical microscopy studies. The gamma crystals probably nucleate at a constant rate within the parent alpha crystal and grow in two dimensional structures (Avrami exponent=3). The excellent fitting of the experimental data at Tc=127 and 128°C to a theoretical single stage Avrami model with n=3 did not require an additional two stage model fit on those data for the linear sample of series 1 at those temperatures. However, the single stage model with n=3 did not fit very well at Tc=126°C and 130°C for the linear sample, as a result a two stage model was applied to the experimental data at these two temperatures.

The results of the the experimental data of the samples of series 1 fitted to two stage model are summarized in table 3.6. The two stage model yielded a value of n=3.2 and m=3.3 at 126°C and a value of n=3 and m=3.4 at 130°C, which leads us to conclude that the nucleation and growth mechanism for both the polymorphs are similar as described above for the linear
sample at $T_c = 127$ and $128^\circ$C. A fit of crystallization data at all $T_c$’s of the H-linked samples in series 1 to the two stage model generated a value of $n = 3.8 \pm 0.3$ and $m = 1.8 \pm 0.3$ (as listed in table 3.5). The value of $m$ can be justified considering the fact that the gamma crystallographic form can nucleate and grow within the parent alpha or parent gamma crystal, assuming that gamma develops as independent crystals without alpha form. Therefore, the growth of gamma crystal may be restricted to single dimension, forming rodlike structures and yielding a value of $m = 2$ ($1.8 \pm 0.3$). For an ideal heterogeneous nucleation where the crystals grow to form spherulites, the value of $n$ would be 3 (as seen for the linear sample in this series).

Table 3.6 contains value of the two stage parameters, the rate constants of formation and level of crystallinity. From table 3.6 it is evident that at the temperature range studied the H-linked samples exhibit around 55-60% of gamma polymorphic form. The study of the kinetic evolution of the polymorphic form in the specified temperature range of 126-136$^\circ$C suggested that within this $T_c$ both polymorphic forms are present from the initial level of transformation. Therefore, the possibility of gamma crystallites nucleating directly from the melt at a constant rate can not be ruled out., and for the H-linked samples of series 1 at all $T_c$’s the Avrami exponent of the first stage can be expected to yield a value of $n = 4$ associated with a sporadic nucleation and growth of the $\gamma$ phase.

The results of the two stage model fit to the experimental data of the samples of series 2 are summarized in table 3.7. A value of $n$ between 3 and 4 is obtained for the linear sample of series 2 and it steadily decreases with increase in the isothermal crystallization temperature. Optical microscopy studies evidenced that the supermolecular structure (figures are in the morphology section) of this sample was spherulitic at the temperature range studied. This might suggest that at higher undercoolings (lower $T_c$) the mechanism of nucleation is homogenous which slowly changes to heterogeneous nucleation with increase in $T_c$. Similar arguments were reported$^{176}$ earlier in order to interpret the analysis of the experimental data for isothermal crystallization of isotactic polypropylene studied using DSC. It was also suggested by Janimac, et. al$^{177}$ that the change in the value of $n$ with change in crystallization temperature may be related to several factors; such as decreasing of supercooling, changes from heterogeneous to homogenous nucleation, and initiation of the secondary crystallization processes.
Table 3.6 Results of 2-stage Hillier model fits (Series 1). The table contains the specified crystallization temperature, $T_c$, the data for which was fitted to obtain the two parameters $m$ and $n$. The respective rate constant of the two polymorphs ($K_\alpha$ and $K_\gamma$) along with the content of alpha phase ($w_\alpha$) is also provided in the table. The last column lists the standard deviation of the experimental data from the model, and is a good indicator of the applicability of the model to experimental data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$w_\alpha$</th>
<th>$n$</th>
<th>$K_\alpha \times 10^3$ (min$^{-n}$)</th>
<th>$m$</th>
<th>$K_\gamma \times 10^3$ (min$^{-m}$)</th>
<th>SSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>126</td>
<td>0.55</td>
<td>3.2</td>
<td>0.12219</td>
<td>3.3</td>
<td>0.6602</td>
<td>0.00819</td>
</tr>
<tr>
<td>(Linear)</td>
<td>127</td>
<td>0.55</td>
<td>3.0</td>
<td>0.0487</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>0.54</td>
<td>3.0</td>
<td>0.0209</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.53</td>
<td>3.0</td>
<td>0.0086</td>
<td>3.4</td>
<td>0.0096</td>
<td>0.00033</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>128</td>
<td>0.45</td>
<td>4.1</td>
<td>3.838</td>
<td>2.0</td>
<td>133.41</td>
<td>0.00017</td>
</tr>
<tr>
<td>(200 ppm)</td>
<td>130</td>
<td>0.46</td>
<td>4.0</td>
<td>0.557</td>
<td>2.1</td>
<td>40.69</td>
<td>0.00014</td>
</tr>
<tr>
<td></td>
<td>132</td>
<td>0.46</td>
<td>3.9</td>
<td>0.08626</td>
<td>2.0</td>
<td>60.321</td>
<td>0.00031</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>0.46</td>
<td>3.5</td>
<td>0.02176</td>
<td>1.5</td>
<td>11.847</td>
<td>0.00984</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>130</td>
<td>0.40</td>
<td>4.0</td>
<td>66.018</td>
<td>2.0</td>
<td>300.04</td>
<td>0.00122</td>
</tr>
<tr>
<td>(375 ppm)</td>
<td>132</td>
<td>0.41</td>
<td>3.9</td>
<td>9.7353</td>
<td>2.0</td>
<td>65.36</td>
<td>0.00181</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>0.42</td>
<td>3.7</td>
<td>1.8362</td>
<td>1.9</td>
<td>27.276</td>
<td>0.00142</td>
</tr>
<tr>
<td></td>
<td>136</td>
<td>0.42</td>
<td>3.7</td>
<td>0.31782</td>
<td>2.1</td>
<td>8.2867</td>
<td>0.00095</td>
</tr>
</tbody>
</table>

Figure 3.30 2-Stage Hillier model fits for samples of series 2  (Solid line represents experimental data and dashed line represents the fit with equation 3.14)  (a) IPP291K1, (b) HLIPP275K1, (c) HLIPP283K1 and (d) HLIPP247K1
Figure 3.30 – continued
The nucleation of PP is mostly considered to be heterogeneous because it contains impurities such as catalyst residues and additives; however, considering a mechanism of heterogeneous nucleation developing into spherulitic morphology the value of n has been obtained between 3 and 4 in one of the previous reports on isothermal crystallization of polypropylene. The value of m for the linear sample is either 2 or 3 which follows our initial expectations for the expected m values for gamma crystals. The H-linked samples exhibit consistent values of n and m in the temperature range studied. The value of n = 3.9 ± 0.4 and the value of m = 3.1 ± 0.4 (except at low Tc’s for each of the samples, where m=2). The higher value of n close to 4 may be explained following the similar argument given for the observed n values of H-linked samples in series 1, whereas the observed value of m follows our initial expectations (for either m=2 or 3).
Table 3.7 Results of 2-stage Hillier model fits (Series 2)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tc (°C)</th>
<th>wα</th>
<th>n</th>
<th>( K_α \times 10^3 ) (min(^n))</th>
<th>m</th>
<th>( K_γ \times 10^3 ) (min(^m))</th>
<th>SSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP291K1 (Linear)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>0.56</td>
<td>3.9</td>
<td>0.487</td>
<td>3.1</td>
<td>8.900</td>
<td>0.00114</td>
<td></td>
</tr>
<tr>
<td>126</td>
<td>0.56</td>
<td>3.7</td>
<td>0.904</td>
<td>3.2</td>
<td>1.649</td>
<td>0.00048</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>0.56</td>
<td>3.4</td>
<td>0.024</td>
<td>2.2</td>
<td>5.6074</td>
<td>0.00418</td>
<td></td>
</tr>
<tr>
<td>HLIPP275K1 (50 ppm)</td>
<td>120</td>
<td>0.58</td>
<td>3.7</td>
<td>23.365</td>
<td>3.0</td>
<td>175.52</td>
<td>0.000693</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>0.57</td>
<td>3.6</td>
<td>0.65129</td>
<td>2</td>
<td>42.833</td>
<td>0.00137</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>0.56</td>
<td>3.7</td>
<td>0.0784</td>
<td>2.9</td>
<td>2.748</td>
<td>0.000674</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>0.55</td>
<td>3.5</td>
<td>0.0201</td>
<td>2.7</td>
<td>1.6524</td>
<td>0.001707</td>
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<tr>
<td>HLIPP283K1 (100 ppm)</td>
<td>124</td>
<td>0.57</td>
<td>4.1</td>
<td>6.166</td>
<td>2.0</td>
<td>375.51</td>
<td>0.001411</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>0.55</td>
<td>4.0</td>
<td>0.7025</td>
<td>3.2</td>
<td>14.671</td>
<td>0.000991</td>
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<tr>
<td></td>
<td>128</td>
<td>0.54</td>
<td>3.9</td>
<td>0.0814</td>
<td>3.5</td>
<td>1.394</td>
<td>0.001127</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.54</td>
<td>3.9</td>
<td>0.06512</td>
<td>3.5</td>
<td>4.2833</td>
<td>0.00137</td>
</tr>
<tr>
<td>HLIPP247K1 (200 ppm)</td>
<td>124</td>
<td>0.48</td>
<td>4.1</td>
<td>3.7375</td>
<td>2.0</td>
<td>227.73</td>
<td>0.000695</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>0.49</td>
<td>4.3</td>
<td>0.30378</td>
<td>3.5</td>
<td>12.727</td>
<td>0.008406</td>
</tr>
<tr>
<td></td>
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<td>0.49</td>
<td>4.1</td>
<td>0.0444</td>
<td>3.5</td>
<td>1.45</td>
<td>0.000446</td>
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<tr>
<td></td>
<td>130</td>
<td>0.50</td>
<td>3.9</td>
<td>0.00833</td>
<td>2.9</td>
<td>0.95</td>
<td>0.000395</td>
</tr>
</tbody>
</table>

From the isothermal crystallization analysis it can be concluded that the crystallization of linear samples of series 1 proceeds through a heterogenous nucleation and ultimately forms spherulitic structures (since a value of n=3 fits well to the experimental data). However, the analysis for H-linked samples suggest that the addition of diene to the linear sample of series 1 causes a change in the mode of nucleation to homogeneous instead of heterogeneous and geometry of structures that evolve on crystallization. Unlike the linear sample, a clear two stage crystallization kinetics is apparent for the H-linked ones (they have very distinct n and m values, table5). Either, the γ form nucleates homogeneously in second stage from alpha crystals with a one dimension growth (justified by value of m= 2) or it can nucleate during first stage thus
producing a value of $n = 4$ associated with a sporadic nucleation (at constant rate) and subsequent 3 dimensional growth of the $\gamma$ phase. However the model cannot really predict the nucleation and growth mechanism of alpha form in the H-linked samples, thus the model may not be appropriate to predict the crystallization mechanism of two different stages in certain cases.

The data obtained for H-linked samples of series 2, listed in table 3.7, have similar nucleation and growth mode as those of series 1. However, the linear sample of series 2 behaved differently compared to its counterpart of series 1. The linear sample of series 2 also had two distinct steps of crystallization and the mode of nucleation seemed to change from homogenous ($n = 4$, $m=3$) to heterogenous ($n = 3$, $m=2$) with increase in $T_c$.

Agarwal et al.\(^{37}\) applied the single stage Avrami model on the crystallization kinetic data from sheared melt of the same set of samples as in series 1 of present study (figure 3.18). These authors concluded that the linear sample forms oriented spherulitic structures ($n = 3$), whereas the H-linked forms rod/disk like crystals ($n = 1.8$). A steady decrease in the value of $n$ from 3 (for linear) to 1.8 (for sample with highest diene) with increase in diene content under isothermal crystallization condition at 140°C led to the above conclusion.

In contrast, the application of single Avrami model to the isothermal crystallization data from quiescent melt of the same set of samples (series 1) lead to a different result in the present study. The results indicated that the crystals of both the linear and H-linked samples grows with a three dimensional geometry. However, the fit of the experimental data to 2 stage model indicated a resemblance with Agarwal’s result. In the two stage model, the second stage exponent related to gamma growth ($m$), decreased from 3 to 2 with addition of diene. This can be explained based on the fact that the growth of $\gamma$ nuclei is confined and dimensionally restricted within $\alpha$ phase; thus the expected Avrami exponents for the $\gamma$ stage are $m=3$ (2 dimensional growth) or $m=2$ (1 dimensional growth).

### 3.1.2.5 Linear growth rates

Crystallization kinetics can also be studied by measuring the growth rate of supermolecular structures that represent the organization of crystallites into three-dimensional arrays. Spherulite is one of the most commonly observed 3 dimensional supermolecular structure occurring as a result of polymer crystallization. The spherulitic growth rate is given by the
variation of the radius vs. time. Concentration of defects and molar mass are the two main factors controlling the linear growth rates. An increase in defect disrupts the regularity in the polymer chain and decreases the rate of growth whereas an increase in molecular weight increases the entanglement and makes transport of chains to the surface more difficult thereby slowing down the growth rate. It has been demonstrated earlier that an increase in either of the two factors tend to decrease the spherulitic growth rate, although the magnitude of influence of the two factors on the growth rates is different.

The H-linked sample in our study differs from the linear one on account of molecular weight (series 1) as well as level of branching in both the series. Therefore, the study of linear spherulitic growth rate of the two series of samples in a range of Tc (isothermal crystallization) can determine the extent to which the two factors influence the linear growth rate. Additionally, it will be of interest to note whether the magnitude of difference in growth rate on addition of branches and molecular weight conforms to the previous studies or differs widely from them. Molecular mass and crystallization temperature influences the supermolecular structure and high molar mass often limits the organization of supermolecular structure and prevents the spherulite formation. Knowing this, it will be interesting to observe (by optical microscope) the difference in supermolecular or spherulitic structure of the linear and LCB samples as they differ widely in molecular mass. The analysis of growth rate data of the samples of series 2 allowed us to study the effect of the defect content induced by H-link independent of their molar mass.

Isothermal crystallization of the samples in both the series at a certain temperature range (130-140°C) resulted in the development of well formed spherulitic structure, as observed using optical microscope. The linear growth rate of the samples of series 1 and 2 is plotted in figure 3.31 and 3.32 respectively. The linear growth rate of all the samples (linear and H-linked ones) exhibited a similar variation with undercooling i.e. for the three of them there is a decrease in growth rate by about ten times with increasing temperature from 130°C to 140°C (fig 3.31), this observation of growth rate with temperature follows the usual nucleation controlled polymer crystallization behavior.

The growth rate of the sample of series 1 with 200ppm diene remained unchanged with respect to the linear iPP, as observed in figure 3.31. At higher diene contents (375ppm) the growth rate decreases between 50 % and 30 % (table 3.8) in the range of temperature studied. This decrease in growth rate can be associated with a combination of two factors, molar mass
and branching (H-linkages). A small molar mass dependence on the growth rate for metallocene iPP homopolymers has been reported\textsuperscript{74}. There is a difference of 0.15mol\% on the overall defect content, considering the effect of defect contents on the growth rate; this difference is insignificant in reducing the growth rate\textsuperscript{74}.

![Figure 3.31](image.png)

**Figure 3.31** Linear growth rates of samples of series 1.

**Table 3.8** Growth rates of the samples of series 1 at three different Tc

<table>
<thead>
<tr>
<th>Tc</th>
<th>IPP151K1.31 (cm/s)</th>
<th>HLIPP203K1.18 (cm/s)</th>
<th>HLIPP276K1.15 (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>130°C</td>
<td>4.37x10^-6</td>
<td>3.595x10^-6</td>
<td>2.189x10^-6</td>
</tr>
<tr>
<td>135°C</td>
<td>1.275x10^-6</td>
<td>1.182x10^-6</td>
<td>0.611x10^-6</td>
</tr>
<tr>
<td>140°C</td>
<td>0.4302x10^-6</td>
<td>0.385x10^-6</td>
<td>0.2475x10^-6</td>
</tr>
</tbody>
</table>
The decrease in the growth rate of HLIPP276K1.15 could be a consequence of increase in molar mass. In order to probe this possibility the growth rate data of this fraction were corrected to the values that this fraction would have if its molar mass is 150,000 g/mol. The correction is possible because linear growth rates of metallocene iPPs with a fixed defect content (~0.5 mol%) in a range of molecular mass from 86000 to 383000 were given in a previous work\textsuperscript{74}. In the present work the difference in molar mass between the linear and the sample with 375ppm of diene is 125,000g/mol. It was observed that for the same difference in molar mass at a constant defect content the growth rate of a fraction increases by ~5-7\%\textsuperscript{74}. Therefore the G of the sample with 375 ppm content was increased by ~6%. The corrected G data for the HLIPP276K1.15 and a line averaging the growth rate data for the linear sample are plotted in Figure 3.31a. The difference between the corrected growth rate of HLIPP276K1.15 and the line averaging that for the linear one was almost identical to the one observed in figure 3.31 between the experimental data for the growth rate of the linear and 375ppm diene containing sample of series 1, figure 3.31.

\textbf{Figure 3.31a}) The points represent the growth rate data of HLIPP276K1.15 corrected to the molar mass of the linear. The line averages the experimental growth rate of the linear sample of series 1.
Thus it can be concluded that it is indeed the difference in molecular weight that caused the small variation in growth rate between the two samples of series 1. The invariance of G with addition of diene between the three samples of series 1, except for the molar mass dependence, follows predictions based on the similar overall defect content, therefore, from the expected similar undercooling.

![Graph of linear growth rates of samples of series 2](image)

**Figure 3.32** Linear growth rates of samples of series 2

Following series 1, the growth rates of the second series exhibited a similar variation with undercooling (the rate decreases with increase in temperature, figure 3.32). In series 1 the molar mass increases proportionally to the diene addition, therefore, the combined effect of molar mass and branching reduces the growth rate to a greater extent compared to samples of series 2. In
series 1 we observe that the growth rate of highest diene content sample (HLIPP276K1.51) decreases by about 50% compared to the linear one at any isothermal crystallization temperature. In series 2 the sample with highest diene content has the lowest molar mass (though the difference in molar mass of the four samples in this series is negligible), and in contrast to the series 1 there is no relation between the molar mass and amount of diene addition in the series 2. The influence of diene on the growth rate is also expected to be negligible for series 2 as the amount of diene added is even less than that of series 1.

The samples of series 2 have similar molar mass, constant overall defect content and negligible influence of diene on the growth rate. A combination of these three factors is responsible for the very little difference observed in the growth rate of the samples studied in a range of crystallization temperature, Tc (131-140ºC) of series 2. This fact is evident from table 3.9 where the absolute value of growth rate data for the 4 samples of series 2 is compared at 3 different Tc’s. Negligible variation of growth rate is observed with addition of diene at same undercooling.

Analysis of the overall crystallization data led to the conclusion that owing to large difference in nucleation density the diene containing samples of series 1 have much higher crystallization rate compared to the linear one. However the addition of diene did not seem to affect the nucleation of the samples of series 2 considerably, and therefore the difference in magnitude of the overall crystallization rate was much moderate among the linear and H-linked samples of series 2. The analysis of the growth rate data also indicates that the nucleation density mostly affects in the molecular characteristics of series 1, as the growth rate of linear and highly nucleated samples of series 1 is different, but the samples of series 2 have minimal differences in the growth rate at a fixed Tc.

### Table 3.9 Growth rates of the samples of series 2 at three different Tc

<table>
<thead>
<tr>
<th>Tc</th>
<th>IPP291K1 (cm/s)</th>
<th>HLIPP275K1 (cm/s)</th>
<th>HLIPP283K1 (cm/s)</th>
<th>HLIPP247K1 (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>131ºC</td>
<td>2.87x10^{-6}</td>
<td>3.44x10^{-6}</td>
<td>2.72x10^{-6}</td>
<td>2.56x10^{-6}</td>
</tr>
<tr>
<td>135ºC</td>
<td>1.03x10^{-6}</td>
<td>1.243x10^{-6}</td>
<td>1.025x10^{-6}</td>
<td>1.047x10^{-6}</td>
</tr>
<tr>
<td>137ºC</td>
<td>0.61x10^{-6}</td>
<td>0.7439x10^{-6}</td>
<td>0.6416x10^{-6}</td>
<td>0.6914x10^{-6}</td>
</tr>
</tbody>
</table>
3.1.2.6 Effects of H-links on degree of crystallinity

The degree of crystallinity of iPP is very important in determining the morphological, physical and mechanical properties of the polymer. It has been observed from earlier studies that the overall crystallinity decreases with increase in defect content\textsuperscript{179} and molecular weight\textsuperscript{116}. An increase in the degree of crystallinity makes the polymer more rigid and tough by increasing the modulus. The dependence of modulus on degree of crystallinity in polyethylene indicates that the crystalline network carries much of the elastic energy acquired when the polymer is subjected to stress\textsuperscript{180}. The degree of crystallinity can be obtained from different measurements, such as:

Heat of fusion measured by DSC: From the heat of fusion value the degree of crystallinity can be obtained as \((1-\lambda) = \frac{\Delta H}{\Delta H_U}\), \(\Delta H\) is the measured specific enthalpy of fusion, and \(\Delta H_U\) is the enthalpy of fusion per mol of repeating unit of the infinite size perfect crystal, the value of \(\Delta H_U\) for isotactic polypropylene used is 209 J/g, obtained from literature\textsuperscript{181}.

Density measurement: The mass fraction degree of crystallinity \((1-\lambda)_d\) obtained from density measurements can be expressed as\textsuperscript{182},

\[
(1-\lambda)_d = \frac{(1/\rho_a)-(1/\rho)}{(1/\rho_a)-(1/\rho_c)}
\] (3.15)

the above equation is based on the assumption of a two-phase system, crystalline and amorphous (liquid-like). Here, \(\rho\) is the measured density of the sample, and \(\rho_a\) and \(\rho_c\) are the densities of the completely amorphous and pure crystalline phase, respectively. To determine \((1-\lambda)_d\) at 25°C, the values of \(\rho_a\) and \(\rho_c\) at this temperature need to be specified. The value of \(\rho_a\) can be obtained by extrapolating the specific volume above the melting temperature to room temperature using dilatometry. The value for \(\rho_c\) can be obtained from the unit cell dimensions when the crystal structure is known.

WAXS: This method involves the analysis of a set of discrete crystalline reflections (Bragg spacings) that are superposed upon a broad amorphous halo. To calculate \((1-\lambda)_x\), it is necessary to separate, or deconvolute, the amorphous band from the crystalline reflections. Once the separation has been accomplished, there are several different methods proposed to calculate \((1-\lambda)_x\). In one of the method used by Isasi\textsuperscript{76} the mass fraction of the crystalline and amorphous phase was taken as being proportional to their respective areas. The crystallinity was calculated as,
\[(1-\lambda)_x = \frac{I_c}{I_c + I_a}\]  

(3.16)

$I_c$ is the total scattering intensity from all the crystalline peaks, and $I_a$ is the area of the amorphous halo.

The degree of crystallinity of isotactic polypropylene can also be measured by spectroscopy techniques, i.e. Raman, vibrational (IR) or NMR spectroscopy.

For a polymer the degree of crystallinity can be varied by controlling molecular weight, molecular weight distribution, crystallization temperature and the defect content of the chain. Molecular weight is a key factor influencing polypropylene properties. A low molecular weight has a positive effect on crystallinity, by allowing the chains to rearrange more rapidly, leading to more perfect crystals. The effect of chain entanglement is much more pronounced in case of high molecular weight polymers owing to their larger chain lengths. Many mechanical and dynamic mechanical properties such as impact strength, the energy needed to fracture divided by the cross-sectional area, and moduli are directly dependent on the degree of crystallinity. In isotactic polypropylene the non-crystalline region controls the deformation process\textsuperscript{183}. Therefore, decrease in molecular weight, together with the corresponding increase in the degree of crystallinity, results in an increment of the brittleness of the polypropylene homopolymer. This reduces the impact strength.

Most likely in the H-linked iPP the branches will be rejected from the crystal lattice as a defect, therefore from the comparison between the degree of crystallinity of branched sample with the linear one, it is expected that former will exhibit lower crystallinity under identical crystallization conditions. Additionally, the branched samples have much higher molecular weights (series 1), which tends to increase the entanglements and reduce the degree of crystallinity at a fixed isothermal crystallization temperature compared to the linear counterpart. Other previous studies also demonstrated that above a critical molecular weight of the branch the crystallinity decreases with increasing the branch length, due to the inability of the longer chains to be incorporated in the crystalline structure\textsuperscript{184, 185}. More significantly, by increasing the number of branches, the polymer crystallinity and density can be reduced, since these side chains do not crystallize and are rejected to the amorphous regions of the polymer. A reduced density hence results in a higher flexibility and in an increased ability to absorb and dissipate energy\textsuperscript{186}.
The increase in branching or the molecular weight or the combination of both factors is expected to reduce the crystallinity of an otherwise linear isotactic Polypropylene.

Although the degree of crystallinity is a quantitative concept, different measurement techniques on exactly the same sample do not always yield the same results. Small but significant differences among the methods can be observed. It has been earlier reported\textsuperscript{187,188} that the crystallinity level determined by density of linear polyethylene and of ethylene copolymers is always greater than the value obtained by the enthalpy of fusion. The difference in the measured values can be attributed to the contribution of interphase, for example, the density includes the contribution from the interphase, while the enthalpy of fusion only measures the core crystallinity\textsuperscript{76}.

In the present work crystallinity was examined by two different techniques, namely, DSC and WAXS. Crystallinity values for isothermally crystallized samples of both series are given as a function of $T_c$ in Figures 3.33(DSC) and 3.34(WAXS)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure3.33.png}
\caption{Crystallinity ($X_c$) of samples of series 1 from heat of fusion (DSC) (■) IPP150K1.31 (▲) HLIPP203K1.18 (♦) HLIPP276K1.15}
\end{figure}
Figure 3.34 Crystallinity (Xc) of samples of series 1 from WAXS (■) IPP150K1.31 (▲) HLIPP203K1.18 (♦) HLIPP276K1.15.

Figure 3.35 Crystallinity from WAXS and Heat of fusion (DSC) for series 1 (■) IPP150K1.31 (▲) HLIPP203K1.18 (♦) HLIPP276K1.15. The line represents the point of equal crystallinity measured by the two methods.
As seen from figure 3.33 and 3.34, any trend regarding the variation of crystallinity with diene addition or H-linking is absent. Also the difference between the crystallinity obtained from either method among the three samples at any chosen Tc is within ±5-7%, indicating that there is in reality a minimal difference in the crystallinity of the linear and H-linked and linear samples of series 1. Thus it can be concluded that effect of H-linkages on the degree of crystallinity was minimal. There may not be enough linkages, considering only ppm levels of diene have been added, to influence the crystallinity by increasing the entanglements. However there is a significant difference among the absolute values of the crystallinity obtained from the two methods for each sample at a fixed Tc. The crystallinity obtained from DSC ranges between 45-65% for the three samples studied in the whole interval of Tc (100-150°C), whereas that obtained from WAXS ranges between 70-85% in the same interval of Tc for the three samples.

The degree of crystallinity values obtained from the two different methods (WAXS and DSC) was compared in figure 3.35. It was noted that analysis of WAXS data gave a higher degree of crystallinity than that obtained from heat of fusion measurements. This discrepancy between the two values follows our expectation\(^{76}\) since the crystallinity measured by DSC takes into account only the core crystallinity values (heat of fusion), whereas the crystallinity measured by WAXS incorporates the contribution of the interphase region in addition to the core crystallinity\(^ {81}\), as a result the crystallinity obtained from WAXS is always higher in magnitude than those obtained from DSC under identical crystallization conditions. From the difference in the crystallinity obtained from DSC and WAXS it can be speculated that the samples for the present study contains \(~10-15\%\) of interphase region.

3.1.3 Non-isothermal crystallization Kinetics

Non-isothermal crystallization kinetics has drawn considerable attention in the field of polymer science and engineering since it approaches more closely to the industrial conditions of polymer processing such as extrusion, molding, and melt spinning of synthetic fibers. The analysis of experimental data according to existing theoretical models of isothermal crystallization is well accepted, but the same for non isothermal crystallization is still not uniformed. Practical processes such as industrial synthesis proceed under dynamic, non-isothermal conditions, therefore, it is necessary to extend the isothermal kinetics to non-
isothermal dynamic kinetics for various types of processes in order to understand the relative development of crystallinity with time factors impacting those processes.

The isothermal measurement is only possible when the thermal response time of the measured system is small compared with the rate of the crystallization. Otherwise the process begins to occur before the system reaches the desired temperature. In this case, one should use a thermoanalytical method in which observations of the sample are made under a constant rate of heating or cooling.

The studies on non-isothermal crystallization kinetics originated from the fact that the Avrami equation could not be used for non-isothermal process. To study kinetic parameters for non-isothermal crystallization processes, several methods have been developed. Interestingly, most of the proposed formulations are based on the Avrami equation. Introducing a cooling rate into the Avrami equation, Ozawa first studied the crystallization of poly(ethylene terephthalate) during cooling. From the Ozawa equation, the Avrami exponent and the cooling function for non-isothermal crystallization at given temperatures can be obtained by using DSC curves with several constant cooling or heating rates. Mo and co-workers proposed another non-isothermal equation by combining the Ozawa and the Avrami equations, from which the ratio of the Avrami exponent to the Ozawa exponent and another parameter can be obtained. Other methods to analyze non-isothermal crystallization have been suggested by many authors like Piorkovska, Lambrigger and Spruiell.

The detailed study of the non-isothermal crystallization of polyethylene, PE, was conducted by Nakamura and coworkers. They studied the non-isothermal kinetics for high density polyethylene, HDPE, by detecting the changes in crystallinity by X-ray scattering and measuring the integrated intensity of the 2θ range under various cooling conditions. The change in crystallinity was analyzed by the theoretical treatment they developed. The agreement with theoretical values was satisfactory, even beyond the range of primary crystallization. Supaphol and Spruiell analyzed the non-isothermal bulk crystallization kinetics for two fractions of HDPE, with Mw values of 101 000 and 77 000, by a modified light-depolarizing microscopy technique, using cooling rates up to 2500ºC/min. They found that the bulk crystallization kinetics is a strong function of cooling rate. The lower molecular mass polymer crystallized slightly faster than the higher molecular mass one over the whole range of undercooling studied. This suggested that the low molecular mass HDPE has a higher molecular mobility than the one with
higher $M_w$. During crystallization, the molecules of the sample with low $M_w$ could dissociate themselves from the entangled-melt more easily, resulting in less time required to complete the crystallization process. Mandelkern and coworkers\textsuperscript{196} studied the morphology of linear and branched polyethylenes crystallized under controlled non-isothermal conditions. They proved that various morphological forms could develop and these could be produced by systematically changing molecular mass, concentration of branch groups and quenching temperature.

Eder and Wlochowicz\textsuperscript{197} first found out that the crystallization of PP followed the Ozawa equation. Paukkeri and Lehtinen\textsuperscript{198} analyzed several fractions of isotactic polypropylene with different degrees of isotacticity. They proved that for molecular mass, $M_w$, ranging from $2.2 \times 10^4$ to $9.5 \times 10^5$; isotacticity was the main parameter determining the crystallization peak temperature and crystallinity, whereas molecular mass had a much less pronounced effect on crystallization rates and almost no influence on crystallinity. Lim and Lloyd\textsuperscript{199, 200} studied the overall non-isothermal crystallization kinetics for nucleated and non-nucleated iPP, as it crystallized from the melt in blends with dotriacontane ($C_{32}H_{66}$). The nucleating agent used was adipic acid. The crystallization peak temperatures for filled samples were higher than those of unfilled samples, indicating that adipic acid was a good nucleating agent for iPP. The difference between the onset and the peak temperatures was taken as a measure of the overall crystallization rate. The non isothermal crystallization for isotactic polypropylene has been also followed by various different methods in literature\textsuperscript{201,202}.

Similar to the trend observed in case of isothermal crystallization for branched polycaprolactones\textsuperscript{73}, the non isothermal crystallization\textsuperscript{203} of same set of samples also demonstrated that relative to the linear sample, the non isothermal crystallization rate were retarded for all branched samples except for the one with fewer branches. The probable cause was attributed to the difference in architectural feature as well as chain mobility.

The Ozawa\textsuperscript{189} and Nakamura\textsuperscript{194} theories are basic in analyzing non-isothermal crystallization kinetics. In the theoretical treatment of the process, Ozawa made the following assumptions:

i) The nucleation mode and growth geometry does not change with temperature at a fixed cooling rate.

ii) The variation of fold length of polymer chain with dynamic cooling is neglected.

iii) Slow secondary crystallization, following the primary one is also neglected.
According to Ozawa theory, the degree of conversion at temperature $T$, $X(T)$, can be calculated as:

$$-\ln[1-X(T)] = \frac{K^*(T)}{a^n}$$

(3.17)

Where $a$ is the cooling rate, $n$ is the Avrami exponent and $K^*$ is the cooling crystallization function. $K^*$ is related to the overall crystallization rate and indicates how fast crystallization occurs\textsuperscript{204}.

From Eq. (3.17) it follows:

$$\ln\{ - \ln[1-X(T)] \} = \log K^*(T) - n \log a$$

(3.18)

A straight line should be obtained by plotting the left term of Eq. (16) versus $\log \chi$, and the kinetic parameters $n$ and $K_p$ can be derived from the slope and the intercept, respectively.

The most interesting feature of the Ozawa method is the possibility to compare the results of crystallization during continuous cooling with those obtained by means of the Avrami equation under isothermal conditions. As this treatment requires values of relative crystallinity at a given temperature for different cooling rates, the temperature range over which the analysis can be applied can be very narrow. Moreover, the constant cooling rates used in this method may cause problems in modeling the development of crystallization during polymer processing.

In the present work the non-isothermal crystallization of the H-linked iPP samples was investigated using Ozawa’s model and the kinetic parameters ($n$) thus obtained were compared with those determined from the Avrami analysis of isothermal crystallization, this may help to infer the effect of different crystallization conditions on the nature and geometry of the crystals, and the validity of Ozawa analysis for iPP and H-linked iPP.

The three samples of series 1 were chosen for studying the non isothermal crystallization kinetics. Eleven different cooling rates (1, 2, 4, 6, 8, 10, 12, 16, 20, 25, 30\textdegree C/min) were used to crystallize these samples dynamically from their melt.

The crystallization exotherms of all the three samples of series 1 at 11 different rates are shown in figures 3.36-3.38. Exotherms for the linear sample IPP150K1.31 (figure 3.36) and for the H-linked isotactic polypropylenes with 200 and 375 ppm diene (figure 3.37 and 3.38) are shown respectively.
Figure 3.36 Exotherms obtained at different cooling rates for IPP150K1.31

Figure 3.37 Exotherms obtained at different cooling rates for HLIPP203K1.18
The peak crystallization temperatures (Tc) for all the systems shift to lower temperatures with increasing cooling rate (fig 3.36-3.38). At slow cooling rates, there is sufficient time to activate nuclei at higher temperatures. On the contrary, at faster cooling rates, the activation of nuclei occurs at lower temperatures. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at slower scanning rates. Another important feature to note from the above figures is that at a fixed cooling rate the crystallization peak temperature (Tc) increases with increase in diene content suggesting an increase in the rate of crystallization in parallel with diene addition. A similar trend was observed in figure 3.1 of our earlier studies of isothermal crystallization with this series.

The curves representing the relative degree of crystallinity, Xc, as a function of temperature are obtained by integration of the exothermic peak during the nonisothermal scan, and are shown in Fig 3.39, 3.40 and 3.41 for each of the three samples. The curves had the well-known sigmoidal shape, which suggests that a treatment for nonisothermal data based on Avrami analysis might be applicable.
Figure 3.39 Sigmoidal curves obtained following Ozawa’s analysis for non-isothermal crystallization from the melt for IPP150K1.31 at indicated cooling rates

Figure 3.40 Sigmoidal curves obtained following Ozawa’s analysis for non-isothermal crystallization from the melt for HLIPP203K1.18 at indicated cooling rates
The sigmoidal curves (figures 3.39-3.41) are characterized by a fast ‘primary’ process during the initial stages and by slower ‘secondary’ processes during the later stages. During the nonisothermal process, the crystallization is enhanced as temperature decreases. This is attributed to the strong temperature dependence of the nucleation and the growth parameters. In later stages large fraction of crystallinity develops by slower, secondary kinetic processes.

Values of the amorphous fraction at a given temperature are taken from these plots and represented versus cooling rates in figures 3.42 for the linear and in figures 3.43 and 3.44 for samples containing increasing amount of diene respectively. The double logarithm of the amorphous fraction $\ln(-\ln[1- X(T)])$ at constant temperature is plotted as a function of the cooling rate, $a$, for each of the samples. According to equation (3.18), the data corresponding to each temperature should be a straight line. The slope provides the Avrami exponent and the intercept determines the value of the cooling crystallization function.
Figure 3.42 Plot of ln[-ln(1-Xc)] vs ln a at various temperatures for IPP150K1.31

Figure 3.43 Plot of ln[-ln(1-Xc)] vs ln a at various temperatures for HLIPP203K1.18

Figure 3.44 Plot of ln[-ln(1-Xc)] vs ln a at various temperatures for HLIPP276K1.15
Figures 3.42-3.44 are also known as Ozawa plot. It is noted that the plots are straight lines. The data corresponding to linear and H-linked isotactic polypropylenes in a temperature range of ~100-130°C, then, conforms with the theoretical treatment of Ozawa. Consequently, equation (3.18) can be used to calculate the Avrami exponents of non-isothermally crystallized iPP. The Avrami kinetic parameters and the $r^2$ (regression coefficient) values, indicating the goodness of the data fitting, were obtained from the best fits. These parameters are summarized in Table 3.10, for all the three samples of series 1.

Table 3.10 Non isothermal crystallization kinetics based on Ozawa analysis for iPP samples of series 1.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>n</th>
<th>$K^*$(°C/MIN)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31 (0ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>3.4</td>
<td>8.8</td>
<td>0.945</td>
</tr>
<tr>
<td>104</td>
<td>4</td>
<td>9.7</td>
<td>0.945</td>
</tr>
<tr>
<td>106</td>
<td>4.1</td>
<td>8.5</td>
<td>0.95</td>
</tr>
<tr>
<td>108</td>
<td>4</td>
<td>7.2</td>
<td>0.97</td>
</tr>
<tr>
<td>110</td>
<td>3.8</td>
<td>5.6</td>
<td>0.997</td>
</tr>
<tr>
<td>112</td>
<td>3.2</td>
<td>2.9</td>
<td>0.953</td>
</tr>
<tr>
<td>114</td>
<td>3.5</td>
<td>2</td>
<td>0.98</td>
</tr>
<tr>
<td>115</td>
<td>2.761</td>
<td>0.423</td>
<td>0.989</td>
</tr>
<tr>
<td>HLIPP203K1.18 (200ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>7.1</td>
<td>20.6</td>
<td>0.99</td>
</tr>
<tr>
<td>114</td>
<td>5.3</td>
<td>13.7</td>
<td>0.934</td>
</tr>
<tr>
<td>116</td>
<td>4.3</td>
<td>9.6</td>
<td>0.997</td>
</tr>
<tr>
<td>118</td>
<td>5.2</td>
<td>10.2</td>
<td>0.995</td>
</tr>
<tr>
<td>120</td>
<td>5.3</td>
<td>8.6</td>
<td>0.993</td>
</tr>
<tr>
<td>122</td>
<td>5</td>
<td>5.9</td>
<td>0.995</td>
</tr>
<tr>
<td>124</td>
<td>4.4</td>
<td>2.7</td>
<td>0.977</td>
</tr>
<tr>
<td>HLIPP276K1.15 (375ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>4</td>
<td>12.1</td>
<td>0.934</td>
</tr>
<tr>
<td>116</td>
<td>4.4</td>
<td>12.1</td>
<td>0.917</td>
</tr>
<tr>
<td>118</td>
<td>4.3</td>
<td>10.8</td>
<td>0.997</td>
</tr>
<tr>
<td>120</td>
<td>4.6</td>
<td>10</td>
<td>0.955</td>
</tr>
<tr>
<td>122</td>
<td>3.6</td>
<td>6.7</td>
<td>0.9999</td>
</tr>
<tr>
<td>124</td>
<td>3.7</td>
<td>5.7</td>
<td>0.9629</td>
</tr>
<tr>
<td>128</td>
<td>3.6</td>
<td>2.3</td>
<td>0.9999</td>
</tr>
</tbody>
</table>
In general, the Ozawa crystallization rate constant $K^*$ (cooling crystallization function) is found to decrease with increasing temperature as it normally would for crystallization in the nucleation-controlled region, suggesting a slower cooling rate at higher temperature. Also in accordance with the results obtained for isothermal crystallization kinetics (Avrami analysis) the rate constant for non isothermal crystallization increases with increase in diene content at a fixed temperature, indicating higher rate of crystallization with addition of diene.

It is also observed that $n$ displays a wide range of values from ~3 to 7, and decreases as the crystallization temperature decreases. The experimental data for the linear iPP sample, analyzed with the Ozawa theory, showed a transition between heterogeneous and homogeneous nucleation at about 110°C. From 104 to 110°C, the Avrami exponent $n$ was close to 4, which corresponded to homogeneous nucleation and three-dimensional growth of the crystallites, whereas in the 110–115°C temperature range, $n$ close to 3 was found and this was attributed to heterogeneous nucleation and three-dimensional growth. Previously, in the temperature range 107–120°C, Hammami et al. calculated $n$ for iPP= 3$^{205}$. The isothermal crystallization for this sample was too fast below 120°C and it could be only analyzed at temperatures above 120°C. Avrami analysis at 126 and 127°C for the isothermal crystallization kinetics fitted the experimental results very well for a value of $n$ corresponding to 3 suggesting a heterogeneous 3 dimensional nucleation similar to what is observed for non isothermal crystallization kinetics above 110°C.

From the optical micrograph study the nucleation appeared to be instantaneous at all the crystallization temperatures and the growth was 3 dimensional (formed spherulites) for all the three samples, accordingly a value of Avrami exponent close to 3 is expected. The values of the $n$ obtained from analysis of non isothermal kinetics coincided with our expectations for the linear sample especially as the crystallization temperature increased.

As seen from table 3.10 the exponent obtained for the diene containing sample are much higher especially for the one with 200ppm diene. In the temperature range of 112-124°C the value of $n$ varies between 4-7. Value of $n$ above 4 does not conform to any physical interpretation of nucleation mode and growth, and, as seen from the table none of the values of $n$ obtained at different crystallization temperatures for HLIPP203K1.18 lie below 4. Isothermal crystallization analysis (section 3.1.2.4) suggested that secondary crystallization plays an important role in the overall crystallization kinetics of the two series of samples. Single stage
Avrami model was not sufficient to fit the experimental data. However, using Hillier’s\textsuperscript{164} two stage model the data was correlated better with the physical behavior of the samples. At higher crystalline volume fractions, the effects of impingement, truncation of spherulites and secondary crystallization become very important and decrease the overall crystallization rate. Ultimately, the value of n is reduced. It has been observed previously that when the secondary crystallization is appreciable (for polyethylene)\textsuperscript{197} then the Ozawa analysis may not be valid. Ozawa neglected secondary crystallization in deriving the theory and as pointed out by Hillier\textsuperscript{Error! Bookmark not defined.164}, false value of n might be obtained if the slow secondary crystallization is neglected in an isotherm.

The theory of Ozawa neglects several other factors affecting the rate of non-isothermal crystallization. For example, homogenous and heterogeneous nucleation has been observed for some polymers, each in different temperature ranges. Further, a constant value of n is also assumed throughout the dynamic process. These factors probably result in the inadequacy of the Ozawa equation universally for each case of dynamic crystallization in polymers and variation of the Ozawa exponent with temperature.

3.1.4 Analysis of the temperature coefficient of the crystallization kinetics

Similar to low molecular weight species the crystallization of polymers is governed by nucleation and growth process. In general two different types of nucleation process are operative, one is the required initiation of the crystallization, termed primary nucleation and the second is the growth by a process of secondary nucleation. A strong negative temperature coefficient is observed in the vicinity of the equilibrium melting temperature and crystallization can only be carried out at temperatures well below melting temperatures, i.e. large undercoolings. Moreover a maximum is observed in the rate of crystallization when crystallization is carried out over an extended temperature range. Close to the glass transition temperature a significant retardation in the crystallization rate takes place due to restricted mobility of the segments of the chain.

Nucleation theory has been important in analyzing and understanding the kinetics of isothermal crystallization from the melt and the temperature coefficient of this process. The temperature dependence of the crystallization rate follows the Turnbull Fisher equation\textsuperscript{147}.

\[
N = N_0 \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{\Delta F^*}{RT}\right)
\]  
(3.18)
According to this equation the crystallization rate is explained in terms of two competing processes: segmental transport and free energy change for nucleation. At high crystallization temperature, the rate of nucleation becomes slow whereas the mobility of chains is high and viscosity is low. Therefore, the process at these temperatures is nucleation controlled, as the temperature is lowered the viscosity increases and rate of nucleation is increased due to favorable thermodynamic conditions. As the temperature is lowered further towards the glass transition temperature the viscosity of the system is increased and this makes the transport of polymer chains difficult across the phase boundary to the crystal growth surface. Thus, the process at temperatures close to glass transition is diffusion controlled. Nucleation occurs between equilibrium melting temperature and glass transition temperature and the rate of crystal growth shows a maxima somewhere between these two temperatures as found experimentally in many systems.\textsuperscript{206,207,208,209,210} There are few polymers (e.g. polypropylene) that do not show a maximum in the rate under these conditions since in these cases sufficiently low crystallization temperature cannot be attained. At low Tc the rate becomes too fast to be registered using experimental available techniques in order for a maximum to be observed.

In equation (3.18) the terms \( \exp\left(-\frac{E_D}{RT}\right) \) and \( \exp\left(-\frac{\Delta F^*}{RT}\right) \) are known as transport term and nucleation term respectively. The transport term is the probability that in the local transport process a chain segment of critical length will reach the surface of the crystal, whereas the nucleation term, represents the probability that the surface nucleus will reach a critical size. As mentioned earlier, once the polymer approaches the glass transition temperature (Tg) crystallization becomes retarded, the Arrhenius activation term that is used at other temperatures fails at 50-80°C above the Tg.\textsuperscript{209} In this temperature range, quite commonly \( E_D \) is taken as the William, Landel and Ferry (WLF) activation energy for viscous flow of amorphous polymers.\textsuperscript{211} In this case \( E_D \) is taken as

\[
E_D = \frac{U^* T}{(T - T_\infty)}
\]

(3.18a)

where \( U^* = C_1 C_2 \), \( C_1 \) and \( C_2 \) are constants, \( T_\infty = T_g - C_2 \), is the temperature below which the viscosity is infinite. At this temperature the required segmental motion becomes infinitesimally slow.

The expression for the free energy of forming a small nucleus from the melt (\( \Delta F^* \)) depends on the type of geometry of the initial nucleus. A cylinder is taken as representing a three
dimensional nucleus, as shown in figure 3.45. It consists of \( \rho \) polymer chains aligned parallel to the length of the cylinder, each having \( \xi \) repeating units.

![Schematic representation of 3 dimensional nucleus.](image)

Figure 3.45 Schematic representation of 3 dimensional nucleus.

The expression of \( \Delta F \) is composed of two terms, the first is the bulk free energy of fusion characterizing the crystalline phase of finite size, and the second, of opposite sign, is the term representing the excess surface free energy contributed by the interfaces present.

The free energy change in forming this cylindrically arranged crystalline array of \( \xi \) units in length and \( \rho \) units in base for a pure system with \( N \) molecules, each comprised of \( x \) repeating units is given by

\[
\Delta F = 2\pi^{1/2} \rho^{1/2} \xi \sigma_u + 2 \rho \sigma_e - \xi \rho \Delta F_u - RT \left( \frac{xN}{x} \ln \left( 1 - \frac{\xi \rho}{xN} \right) - \rho \ln \left( \frac{x - \xi + 1}{x} \right) \right)
\]

(3.19)

\( \sigma_e \) and \( \sigma_u \) are the basal and lateral surface free energy respectively. The free energy of fusion per repeating unit of a chain of infinite molecular weight is given by \( \Delta F_u \). The first two terms in
equation 3.19 represent the positive contribution to the free energy from the surfaces present, the third term represents the free energy of fusion of the crystals. The last two terms are introduced for the finite chain length of the molecules, here the first term expresses the entropy gain owing to increased volume available after melting and the last term signifies the portion of the chain units of a given molecule that are involved in the nucleus.

A Gibbs type nucleus is shown in figure 3.46

The expression for the formation of a Gibbs type nucleus is given by

\[ \Delta F = 2\zeta \sigma_u + 2\rho \sigma_c - \xi \rho \Delta F_u + \frac{RT}{x} \xi \rho - RT \rho \ln \frac{x - \xi + 1}{x} \]  

(3.20)

As \( x \) approaches infinity (For \( M_w > 30,000 \)) the last two terms of equation (3.20) become zero and the equation simplifies to

\[ \Delta F = 2\zeta \sigma_u + 2\rho \sigma_c - \xi \rho \Delta F_u \]  

(3.21)

Crystallization of homopolymers from bulk or solution results in the formation of lamellar like crystallites. In such crystals the chain axes are oriented normal to the basal plane of
the lamellae. A secondary nucleation theory involving growth has been proposed\textsuperscript{213, 214} where it was assumed that the chains within the nucleus are regularly folded. In this theory a Gibbs type of nucleus was selected to represent the growth nucleus. Regularly folded chains are deposited on the face of an existing crystallite (figure 3.47). A surface nucleus of length l, thickness b and width a, forms on the substrate and spreads in the direction denoted g. The surface nucleus then completes a layer of thickness b by spreading to the crystal width L, causing the crystal to grow in the G direction.

![Figure 3.47](image)

**Figure 3.47** Model for surface nucleation and growth of chain folded crystal (Adapted from J.D.Hoffman, G.T.Davis and J.I.Lauritzen, 1976, *Treatise on Solid State Chemistry*, Hanny, N.B., Ed., Plenum Press, New York3)

The surface nucleus starts by a polymer segment from the undercooled melt, forming the first stem requiring an energy equivalent to $2b_0l\sigma_u$. The molecule then folds back on itself and starts to crystallize in an adjacent position, as this is the most probable site for reentry after folding. In addition to $2b_0l\sigma_u$, this step requires an additional energy term, $2b_0a\sigma_e$ from the basal surface free energies. By repeating this act the nucleus spreads in the direction g.
The free energy change that is incurred in forming regularly folded chain nucleus from the melt is given by\(^{217}\)

\[
\Delta F = 2b_0/l\sigma_u + 2b_0a\sigma_e - ab_0l\Delta F_u
\]  
(3.22)

The free energy expression given in equation 3.22 contains a saddle point if it is plotted against the dimensions of the critical size nucleus. The coordinates of which can be obtained by setting \(\frac{\partial \Delta F}{\partial l}\) and \(\frac{\partial \Delta F}{\partial a}\) equal to zero. It is then found that

\[1^* = 2\sigma_d/\Delta G_u\]  
and \[a^* = 2\sigma_d/\Delta G_u\], \(1^*\) and \(a^*\) represent the dimensions of a critical size nucleus.

Substituting these in equation (3.22) we get the critical energy for the formation of regularly folded nucleus as

\[
\Delta F^* = \frac{4\sigma_c\sigma_u b_0}{\Delta F_u}
\]  
(3.23)

The free energy of crystallization per unit volume of pure crystal is given as

\[
\Delta F_u = \Delta H_u - T_c\Delta S_u
\]  
(3.24)

Now at \(T_m^0\) \(\Delta F_u\) must be zero (equilibrium conditions), then

\[0 = \Delta H_u - T_m^0\Delta S_u\]  
(3.25)

and \(\Delta S_u = \frac{\Delta H_u}{T_m}\), (assuming that in the temperature range between \(T_m^0\) and \(T_c\), \(\Delta H_u\) and \(\Delta S_u\) is temperature independent), substituting this expression in equation 3.24, \(\Delta F_u\) becomes

\[
\Delta F_u = \Delta H_u - T_c\frac{\Delta H_u}{T_m^0} = \frac{\Delta H_u(T_m^0 - T_c)}{T_m^0}
\]  
(3.26)

or,

\[
\Delta F_u = \frac{\Delta H_u\Delta T}{T_m^0}
\]  
(3.27)
Substituting equation (3.27) in equation (3.23) we get (in the limit of high molecular weight)

$$\Delta F^* = \frac{4b_0 \sigma_c \sigma_u T_m^0}{\Delta H_u \Delta T}$$  \hspace{1cm} (3.28)

A correction factor \( f = \frac{2T_c}{T_m^0 + T_c} \)\(^{216}\) was introduced to account for the variation of heat of fusion with temperature, thus the final expression becomes,

$$\Delta F^* = \frac{4b_0 \sigma_c \sigma_u T_m^0}{\Delta H_u \Delta T f}$$  \hspace{1cm} (3.29)

Substituting \( E_D \) and \( \Delta F^* \) from equations (3.18a) and (3.29) into equation (3.18) we get,

$$N = N_0 \exp(-\frac{U^*}{R(T_c - T_m)}) \exp(-\frac{4b_0 \sigma_c \sigma_u T_m^0}{R \Delta H_u T_c \Delta T f})$$  \hspace{1cm} (3.30)

equation (3.30) can be expressed as

$$N = N_0 \exp(-\frac{U^*}{R(T_c - T_m)}) \exp(-\frac{K_g T_m^0}{T_c \Delta T f})$$  \hspace{1cm} (3.31)

where, \( K_g = Y b_0 \sigma_c \sigma_u / k \Delta H_u \)\(^{217}\), (the value of \( Y \) can be either 2 or 4, detailed discussion is given below)

According to the above equation, a plot of nucleation (or growth) rate (\( \log G \) or \( \log N \)) against the appropriate temperature variable should yield a straight line.

In the late 1960’s, Hoffman and his co-workers applied the nucleation theory to growth rates of polymers like polyethylene, isotactic polystyrene and others observing that there was a considerable deviation of the experimental data for the observed growth rates from the theoretically expected behavior, i.e. a plot of the growth rate against the temperature dependent term, \( 1/T_c \Delta T \), produced a break instead of the expected single straight line with constant slope. The secondary surface nucleation theory was extended to account for these experimental deviations\(^{215, 216}\). Three crystallization regimes were envisaged which were classified according
to the degree of undercooling. Crystallization in each regime is controlled by two factors, secondary nucleation rate \((i)\) and lateral growth rate \((g)\). For high temperature crystallizations the growth rate is allowed to spread across the face of the crystal before the nucleation of next layer \((g>>i)\), and is termed as regime I (figure 3.48a). The growth is given by \(G_I = bL^{217}\), where \(b\) is the thickness of a growth step and \(L\) is the layer width. For regime I,

\[
K_{s,I} = \frac{4b\sigma_u\sigma_T^0}{\Delta H_u k}
\]

\(k\) is the Boltzmann’s constant.

In regime II (figure 3.48b) multiple surface nucleation starts occurring before the previous layer has filled the substrate \((i>>g)\). The growth rate depends on both \(i\) and \(g\) for multiple nucleation, \(G_{II} = b(2ig)^{0.5}\). For regime II,

\[
K_{s,II} = \frac{2b\sigma_u\sigma_T^0}{\Delta H_u k}
\]

Regime III (figure 3.48c) is entered when the niche separation characteristic of the substrate in Regime II approaches the width of a molecular stem. The growth rate is controlled by the nucleation rate, \(G_{III} = bL\).

The temperature coefficient in regime III has the same functionality as that of regime I.

**Figure 3.48** Regimes of crystallization (Adapted from L. Mandelkern, "Crystallization of Polymers", McGraw-Hill Book Company, N.Y., 1964)
The spherulitic growth rates of many polymers have been extensively analyzed with regime theory. These polymers include linear polyethylene\textsuperscript{218,219} \textsuperscript{220}, poly(chlorotrifluoroethylene)\textsuperscript{220}, polydioxolane\textsuperscript{221}, poly (p-phenylene sulphide)\textsuperscript{2} \textsuperscript{222}, and poly (L-lactic acid)\textsuperscript{223} among others.

The regime transition has also been reported for isotactic poly(propylene). Falkai and Stuarts in 1959\textsuperscript{224}, were the first to observe an abrupt upward curvature in the growth rate data with decrease in temperature. Miller and Seeley\textsuperscript{225} pointed out that a strong curvature occurred in i-PP data when the conventional type of plot suggested by nucleation theory was used. Presence of regime III in the temperature coefficient of isothermal crystallization of iPP was first detected by Hoffman\textsuperscript{226} in 1984. Subsequently, in 1990 Cheng S.Z.D. et. al observed all the three regimes in a isotactic PP with low molar mass((\text{Mn}=15,000). However, in the case of high molar mass fractions (300,000) they observed only two regimes, II and III\textsuperscript{227}. Occasionally, data at low undercoolings and for iPP fractions of low molecular mass appear to display a II–I regime transition in addition to the III–II transition most generally found\textsuperscript{228}. Other investigators, such as Haudin\textsuperscript{229} and Marand\textsuperscript{230} and co-workers also observed regime transitions in isotactic poly(propylene) homopolymers.

3.1.4.1 Temperature coefficient analysis applied to H-linked isotactic polypropylenes

The linear growth rates and overall crystallization rates for the two series of samples are are examined using the nucleation theory, as described in the previous section. It has been observed that nucleation theory can be applied successfully to either the overall rate\textsuperscript{31} or growth rate data\textsuperscript{14}. For growth rate equation (3.1) will take the form

$$G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp\left(-\frac{K_s T_m^0}{T_c \Delta T_f}\right)$$ \hspace{1cm} (3.32)

Taking log and rearranging equation 3.32 becomes

$$\ln G + \frac{U^*}{R(T_c - T_\infty)} = \ln G_0 - \frac{K_s T_m^0}{T_c \Delta T_f}$$ \hspace{1cm} (3.33)

For overall crystallization rates the above equation becomes:
\[
\ln\left(\frac{1}{t_{1/2}}\right) + \frac{U^*}{R(T_c - T_m)} = \ln\left(\frac{1}{t_{1/2}}\right)_0 - \frac{K_g T_m^0}{T_c \Delta T_f}
\]  

(3.34)

here, \((1/t_{1/2})\) is the time required to reach the peak crystallization temperature.

The purpose of analyzing the crystallization rate data is to extract structural data of the type of nucleus and crystals that develop in the samples analyzed. The structural data of crystals from LCB iPPs may differ from those of linear iPP. For example, the theory leads to values of the interfacial free energies from the slope of a plot of \(\ln(G \text{ or } 1/t_{1/2}) + \frac{U^*}{R(T - T_\infty)}\) against \(T_m^0/T_\Delta T_f\).

All parameters involved in equation (3.32) need to be chosen carefully for this analysis. The value of the equilibrium melting temperature of the isotactic polypropylene has been controversial for the past few decades, one group reported the value as 186°C, and the other group suggested values between 200-220°C. In the analysis of crystallization rate data of the present work both \(T_m^0\) values (186 and 200°C) was used to check the effect of \(T_m^0\) on the break in transition and on the calculated surface energies. The melting temperature of copolymers relative to those of the parent homopolymers can be derived using classical phase equilibrium theory. From the point of view of crystallization, in addition to various chemical repeating units, structural irregularities like stereo defects, region defects and branch points all behave as copolymeric units when they are incorporated into the chain. For the present study, \(T_m^0\) for the linear and H-linked polypropylenes were obtained using Flory’s theory. The H-linked polypropylenes were treated as copolymers owing to the presence of chain irregularities in the form of stereo and regio defects. It was assumed that the defects do not participate in crystallization.

Flory’s equation is given as,

\[
\frac{1}{T_m^C} = \frac{1}{T_m^0} - \frac{R}{\Delta H_u} \ln X_A
\]  

(3.35)

Here \(T_m^C\) is the equilibrium melting temperature of the isotactic polypropylene homopolymer with defects, \(T_m^0\) is the equilibrium melting temperature of ideal isotactic polypropylene (it is
186°C or 200°C, for the present study). \( \Delta H_u \) is the enthalpy of fusion per mole of repeat unit of the pure isotactic polypropylene (2100cal/mol or 209J/g)\(^{233} \) and \( X_A \) is the mole fraction of crystallizable units for each samples)\(^{234} \) (i.e. for a sample with 1 mol% defect, \( X_A = 1-0.01=0.99 \)). The layer thickness \( b_0 \) is 6.26Å \(^{235} \). The density of polypropylene is taken as 0.945g/cm\(^3\) \(^{236} \).

\( E_D \) is taken as WLF activation energy for viscous flow of polymers. The values of \( U^* \) and \( C_2 \) of most semicrystalline polymers are unknown. Two sets of values, \( U^* = 4120 \text{ cal/mol} \), \( C_2 = 51.6^\circ \text{C} \) and \( U^*=1500 \text{cal/mol} \) and \( C_2=30^\circ \text{C} \) were treated as universal\(^{217} \). In the present case both set of values were used to analyze the crystallization rates, and the surface energy values obtained from both the sets was compared in order to conclude which set gives justified values of interfacial surface energies. The glass transition temperature of polypropylene reported in the literature ranges from -12°C to -15°C \(^{51,237} \). A value of \( T_g = -15^\circ \text{C} \) was employed in analyzing the crystallization kinetics according to the nucleation theory.

Using parameters listed above, the slope of \( \ln G+U^*/R(T_c-T_\infty) \) against \( T_m^0/T_c \Delta T_f \) was used to obtain the value of \( K_g \). Except for the product \( \sigma_c \sigma_u \), the other terms in the expression of \( K_g \) are known from the literature. The lateral surface free energy \( \sigma_u \) was calculated according to Hoffman\(^{238} \).

\[
\sigma_u = \frac{a\Delta H_u l_b}{2l_u C_\infty} \tag{3.36}
\]

Here, \( l_b \) is the C-C backbone length and \( l_u \) the C-C distance as projected along the chain length, \( C_\infty \) is the characteristic ratio of polypropylene chain. Considering alpha phase crystal, the values used for the parameters in equation 3.36 are obtained from the literature, \( a_0 = 5.49\text{Å} \)^\(^{253} \) \( C_\infty = 5.7 \)^\(^{237} \) \( l_b/l_u = 1.42 \)^\(^{237} \)

The interfacial surface free energies can be extracted from the analysis of the slopes assuming that they are not temperature dependent.
Undercooling and molar mass are the two main factors influencing regime transition. The samples in series 1 have similar overall defect content, as a result the major factor influencing the behavior of regime transition will be the difference in their molar mass. In order to investigate the influence of molar mass and H-linkages, nucleation theory was applied to the experimental data for the growth and overall crystallization rates.

### 3.1.4.1.1 Analysis of the temperature coefficient of the overall crystallization rates

The variation of the overall crystallization rates with temperature are analyzed in this section according to equation 3.34.

Different set of parameters ($U^*$, $C_2$ and $T_m^0$) were used to obtain the interfacial surface free energies from analysis of the overall crystallization data of the samples of series 1. The corresponding plots of $\ln(1/ t_{1/2}) + U^*/(R(T_c-T_{\infty}))$ against $T_m^0/T_c\Delta T_f$ for series 1 are also shown in figure 3.49-3.52.

![Temperature coefficient analysis](image)

**Figure 3.49** Temperature coefficient analysis of overall crystallization rate of series 1 with $T_m^0$=200°C, $U^*$= 1500cal/mole, $T_g$ = -15°C, $C_2$ = 30°C, $T_{\infty}$ = -45°C
Figure 3.50 Temperature coefficient analysis of overall crystallization rate of series 1 with $T_m^0=200\,^\circ C$, $U^*=4120\text{cal/mole}$, $T_g=-15\,^\circ C$, $C_2 = 51.6\,^\circ C$, $T_{inf} = -66.6\,^\circ C$

The behavior of samples of series 1 is analyzed with $T_m^0=200\,^\circ C$. The difference between the two figures are the set of $U^*$ and $C_2$ values. The parameters used are written in the legends corresponding to each figure.

The analysis of the overall crystallization rate data according to nucleation theory produced a break instead of a single straight line with constant slope for the diene containing samples. The break is found at $T_c = 132\,^\circ C$ for the sample with 200ppm diene and at $T_c = 135\,^\circ C$ for the sample with 375ppm diene in the temperature range studied (120-140°C). The slight increase in the transition temperature from 132°C to 135°C may be an effect of increasing molecular weight (from 200,000 to 276,000g/mol) as shown in a similar study of polyethylene fractions in a wide range of molecular masses\textsuperscript{239}. For isotactic polypropylene the observed discontinuity can be associated with a regime II-III transition as suggested by previous authors\textsuperscript{237, 229}. The break that would be consistent with a regime I-II is observed in a crystallization temperature range much higher than what is accessible in our experiments (in the vicinity of 150°C)\textsuperscript{228, 227}. However, the slopes ($K_{III}/K_{II}$) lie between 1.2-1.5, which is far below the predicted value of $2\textsuperscript{229, 237}$. The data for the linear sample was analyzed between a
temperature range of 121-132°C, therefore regime II-III transition was not observed in the linear sample. According to previous literature a regime III was assumed for the linear sample in the range of crystallization temperature. The structural parameter ($\sigma_e$) is calculated from the slopes of the figures according to method described in previous section. The data are listed in table 3.11.

**Table 3.11** Values of surface energy (overall) for series 1 samples obtained with $T_m^0=200°C$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Regime</th>
<th>$T_m^0_{cop}$ (°C)</th>
<th>Slope of $\ln(1/(b_0\beta + \sigma_u/(R(T_c-T_m))))$, t (min)</th>
<th>Ratio of slopes $\sigma_u/\sigma_e$</th>
<th>$\sigma_u$ (erg/cm²)</th>
<th>$\sigma_e$ (erg/cm²)</th>
<th>Slope of $\ln(1/(b_0\beta + \sigma_u/(R(T_c-T_m))))$, t (min)</th>
<th>Ratio of slopes $\sigma_u/\sigma_e$</th>
<th>$\sigma_u$ (erg/cm²)</th>
<th>$\sigma_e$ (erg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>III</td>
<td>197.3</td>
<td>1576</td>
<td>1.35</td>
<td>1716</td>
<td>127</td>
<td>1736</td>
<td>1.36</td>
<td>1892</td>
<td>140</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>III</td>
<td>197.55</td>
<td>1476</td>
<td>1.35</td>
<td>1608</td>
<td>119</td>
<td>1639</td>
<td>1.36</td>
<td>1785</td>
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</tr>
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<td>III</td>
<td>197.60</td>
<td>1292</td>
<td>1.25</td>
<td>1408</td>
<td>104</td>
<td>1448</td>
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<td>1577</td>
<td>116</td>
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<tr>
<td></td>
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<td>2255</td>
<td>167</td>
<td>1137</td>
<td></td>
<td>2478</td>
<td>183</td>
</tr>
</tbody>
</table>

**Figure 3.51** Temperature coefficient analysis of overall crystallization rate of series 1 with $T_m^0=186°C$, $U^*_{e}=1500$cal/mole, $T_g = -15°C$, $C_2 = 30°C$, $T_{inf} = -45°C$, $\sigma_u = 13.5$erg/cm²
Figure 3.52 Temperature coefficient analysis of overall crystallization rate of series 1 with \( T_{m0} = 186°C, U^* = 4120\text{cal/mole}, T_g = -15°C, C_2 = 51.6°C, T_{inf} = -66.6°C \)

Table 3.12 Values of surface energy (overall) for series 1 samples obtained with \( T_{m0} = 186°C \)
Data for \( U^* = 1500\text{cal/mole} \) and \( U^* = 4120\text{cal/mole} \) (fig 3.51 and 3.52) (\( \sigma_u = 13.5\text{erg/cm}^2 \))

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>( T_{m0}^{cop} ) (°C)</th>
<th>( U^* = 1500\text{cal/mole}, C_2 = 30°C, T_{inf} = -45°C )</th>
<th>( U^* = 4120\text{cal/mole}, C_2 = 51.6°C, T_{inf} = -66.6°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>III</td>
<td>183.40</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1077 80 1089</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1186 88</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>III</td>
<td>183.62</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1010 75 1030</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1122 83</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>III</td>
<td>183.70</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1389 103 699</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1524 113</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>183.62</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1389 103 699</td>
<td>\begin{align*} \sigma_u \sigma_e \text{ (erg/cm}^4) \end{align*} 1524 113</td>
</tr>
</tbody>
</table>

In figures 3.51 and 3.52 the samples of series 1 are analyzed with a \( T_{m0} = 186°C \). The difference between the two figures are the set of \( U^* \) and \( C_2 \) values. The structural parameter was obtained from the slope. The data are listed in table 3.12. The surface energies calculated from the two different sets of parameters are listed in tables 3.11-3.12. The absolute value of surface energy for each of the samples changed depending on the \( T_{m0} \) used. However, the trend
in variation of the surface energy with diene addition is preserved, i.e., irrespective of the values of \( T_m^0 \) used, it is observed that with addition of diene the fold surface energy decreases marginally (by 15-20ergs/cm\(^2\) from values in regime III). If the values of \( \sigma_e \) obtained from regime II are compared for the two diene containing samples, it is observed that there is also a slight decrease in the surface energy with increasing diene from 200 to 375ppm (see data of tables 3.11 and 3.12).

In our previous paper\(^47\) it was suggested that with increase in gamma content the surface energy decreases owing to less number of chains leaving the crystal surface per unit area, and thereby reducing the surface strain. In the \( \alpha \) phase the distance between the chains at the lamellar interface (\( d_\alpha \)) is identical with the chain distance inside the crystal (\( d_l \)) (figure 3.53a). In \( \gamma \) phase the helices make a 50° angle with the lamellar surface; hence, the distance of the chains (\( d_\gamma \)) at lamellar surface is larger than the chain distance within the crystal (\( d_l \)) (figure 3.53b). Therefore, if \( x \) is the number of chains emerging from the \( \alpha \) phase per square cm, then, \( x \sin 50 \) is the number of chains that will emerge per square cm in the \( \gamma \) phase. The difference between them (\( x - x \sin 50 \)) is 0.23. Hence, we can conclude that, compared to the \( \alpha \) crystal, the existence of non-parallel chain orientations in the \( \gamma \) phase leads to \( \sim 23\% \) less number of chains leaving the crystal surface per unit area. Therefore, the increased surface area available per chain should project a decreased surface strain in the \( \gamma \) crystals.

\[ \text{Figure 3.53a Chains leaving } \alpha \text{ crystal} \]
\[ \text{Figure 3.53b Chains leaving } \gamma \text{ crystal} \]
The same reasoning can be used to explain the observed trend of surface energies listed in table 3.11-3.12. With increase in H-linkages the gamma content increases as evidenced earlier, as a result, the surface energy decreases. The choice of a different set of ‘universal’ constants for the transport term, and different Tm⁰ changed the absolute value of the slopes for each copolymer but not the characteristic linearity of the gradient. The ratio of the slopes and therefore the trend in σₑ was basically not affected by changing Tm⁰.

A wide range of σₑ values for isotactic polypropylene have been reported in the literature. For example, Marand et al.²³⁰ listed σₑ = 146±48 ergs/cm² using Tm⁰ = 212°C, Haudin et al.²²⁹ obtained σₑ = 122 ergs/cm², with Tm⁰ = ~200-212°C, Cheng et al.²²⁷ reported that the values of σₑ lie between 50-70 ergs/cm², with Tm⁰ = 186°C. After a comparison with the reported values it can be concluded that the range of fold surface energy (σₑ) value obtained from the analysis of the overall crystallization data of the iPP samples of series 1 in the present work is within the observed range by other investigators.

The kinetics are also evaluated assuming that the effect of the transport term in the nucleation driven range range for iPP crystallization, is basically constant with temperature, and, hence, negligible. The results of this analysis are shown in figure 3.54.

![Figure 3.54](Image)

**Figure 3.54** Temperature coefficient analysis of overall crystallization rate of series 1 with Tm⁰=200°C, Tg = -15°C, C₂ = 30°C, Tₐₕ = -45°C (Without transport term)
Table 3.13 Values of surface energy (overall) for series 1 samples obtained with Tm\(^0=200°C\), (Without transport term) (\(\sigma_u = 13.5 \text{erg/cm}^2\))

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>(Tm^0_{copt} (^\circ C))</th>
<th>Slope</th>
<th>Ratio of slopes</th>
<th>(\sigma_u\sigma_e (\text{erg}^2/\text{cm}^4))</th>
<th>(\sigma_e (\text{erg/cm}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>III</td>
<td>197.30</td>
<td>1440</td>
<td></td>
<td>1568</td>
<td>116</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>III</td>
<td>197.55</td>
<td>1336</td>
<td>1.33</td>
<td>1455</td>
<td>108</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>III</td>
<td>197.60</td>
<td>1153</td>
<td>1.22</td>
<td>1256</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>197.60</td>
<td>943</td>
<td></td>
<td>2054</td>
<td>152</td>
</tr>
</tbody>
</table>

The results indicate a minimal influence of transport term on the values of the slope and, hence, on the calculated interfacial surface energy. The slope remains almost constant and there is a slight increase (a maximum of 10ergs/cm\(^2\)) in the fold surface energy values with respect to those obtained by using transport term. This increase is expected, since the transport term, \(\exp[-U*/R(Tc-Tinf)]\) would become dominant only at low Tc where the process is diffusion controlled. The occurrence of regime II/III transition of isotactic polypropylene in the right side of the growth rate versus crystallization temperature evidences that crystallization is nucleation controlled, therefore \(U^*\) should have negligible influence on the kinetics.

**Analysis of overall crystallization data of samples of series 2**

The overall crystallization rate data for the samples of series 2 were similarly analyzed according to nucleation theory. As seen in figures 3.55-3.58, the four samples were analyzed in the crystallization temperature range of 118°C-132°C. None of them exhibited a characteristic break observed for the diene containing samples of series 1.

The breaks for series 1 sample were observed above 132°C, as a result it can be speculated that in order to observe breaks in the data we need to follow the crystallization at higher temperatures. However the analysis of at higher Tc was not possible for this series. The defect content being very similar for the two series, it is expected that the data of both the series can be analyzed at similar Tc’s.
Figure 3.55  Temperature coefficient analysis of overall crystallization rate of series 2 with $T_{m^0}=200°C$, $U^*=1500$ cal/mole, $T_g = -15°C$, $C_2 = 30°C$, $T_{inf} = -45°C$

Figure 3.56  Temperature coefficient analysis of overall crystallization rate of series 2 with $T_{m^0}=200°C$, $U^*=4120$ cal/mole, $T_g = -15°C$, $C_2 = 51.6°C$, $T_{inf} = -66.6°C$

However the diene containing samples of series 1 crystallize much faster owing to higher nucleation, therefore the rate of those samples could be followed at higher Tc’s. Moreover, it can be observed from the figure 3.56 that the data for the samples of series 2 almost overlap each other whereas there was a significant difference for the data of samples of series 1. The wide
difference in overall crystallization rates of the diene containing samples of series 1 from its linear counterpart is responsible for this discrepancy. The rate difference is associated with the $\ln(1/t_{1/2})$ term in the y-axis of the figure. Similar to above studies different set of parameters were used in calculating the surface energies. The absolute value of the calculated surface energies changed depending on the set of parameter used, as listed in table 3.14 and 3.15.

Table 3.14 Values of surface energy (overall) for series 2 samples obtained with $T_m^0=200^\circ C$, Data for $U^*=1500$cal/mole and $U^*=4120$cal/mole (fig 3.55 and 3.56) ($\sigma_u=13.5$erg/cm$^2$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>$T_m^0_{cop}$ ($^\circ C$)</th>
<th>$U^* = 1500$ cal/mole, $C_2 = 30^\circ C$, $T_{inf} = -45^\circ C$</th>
<th>$U^* = 4120$ cal/mole, $C_2 = 51.6^\circ C$, $T_{inf} = -66.6^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP291K1</td>
<td>III (as)</td>
<td>198 2143 2335 173 2381 2381 2594 192</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$) $\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>HLIPP275K1</td>
<td>III (as)</td>
<td>198 2188 2384 177 2329 2329 5073 376</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$) $\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>III (as)</td>
<td>198 2054 2238 166 2228 2228 4853 360</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$) $\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>III (as)</td>
<td>198 1990 2168 161 2164 2164 4714 350</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$) $\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$)</td>
<td></td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>III (as)</td>
<td>198 1990 2168 161 2164 2164 4714 350</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$) $\sigma_u \sigma_e$ (erg/cm$^4$) $\sigma_u$ (erg/cm$^2$) $\sigma_e$ (erg/cm$^2$)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.57 Temperature coefficient analysis of overall crystallization rate of series 2 with $T_m^0=186^\circ C$, $U^*=1500$cal/mole, $T_g = -15^\circ C$, $C_2 = 30^\circ C$, $T_{inf} = -45^\circ C$
Figure 3.58 Temperature coefficient analysis of overall crystallization rate of series 2 with $Tm^0=186^\circ C$, $U^*=4120$cal/mole, $Tg=-15^\circ C$, $C_2=51.6^\circ C$, $T_{inf}=-66.6^\circ C$

Table 3.15 Values of surface energy (overall) for series 2 samples obtained with $Tm^0=186^\circ C$, Combined data for $U^*=1500$cal/mole and $U^*=4120$cal/mole (fig 3.57 and 3.58) ($\sigma_u=13.5$erg/cm$^2$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>$Tm^0_{cop}$ (°C)</th>
<th>$U^*=1500$cal/mole, $C_2=30^\circ C$, $T_{inf}=-45^\circ C$</th>
<th>$U^*=4120$cal/mole, $C_2=51.6^\circ C$, $T_{inf}=-66.6^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope $\sigma_x\sigma_u$ (erg/cm$^4$)</td>
<td>$\sigma_u$ (erg/cm$^2$)</td>
<td>Slope $\sigma_x\sigma_u$ (erg/cm$^4$)</td>
</tr>
<tr>
<td>IPP291K1</td>
<td>III (as)</td>
<td>184</td>
<td>1369</td>
<td>1492</td>
</tr>
<tr>
<td></td>
<td>II (as)</td>
<td>184</td>
<td>1369</td>
<td>2983</td>
</tr>
<tr>
<td>HLIPP275K1</td>
<td>III (as)</td>
<td>184</td>
<td>1407</td>
<td>1533</td>
</tr>
<tr>
<td></td>
<td>II (as)</td>
<td>184</td>
<td>1407</td>
<td>3065</td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>III (as)</td>
<td>184</td>
<td>1299</td>
<td>1415</td>
</tr>
<tr>
<td></td>
<td>II (as)</td>
<td>184</td>
<td>1299</td>
<td>2831</td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>III (as)</td>
<td>184</td>
<td>1259</td>
<td>1372</td>
</tr>
<tr>
<td></td>
<td>II (as)</td>
<td>184</td>
<td>1259</td>
<td>2743</td>
</tr>
</tbody>
</table>

From the analysis of overall crystallization data for both the series of samples, it can be concluded that the surface energy values obtained for the samples of series 2 are 30-50ergs/cm$^2$ higher than the samples of series 1, analyzed with same set of parameters. For example if we compare the $\sigma_e$ for linear sample of both the series obtained using same set of parameter, i.e. $Tm^0=186^\circ C$, $C_2=30^\circ C$, and $U^*=1500$cal/mol, we observe that the $\sigma_e$ for the linear sample of series
1 is 80ergs/cm² (table 3.12), and the value of its counterpart in series 2 is 110 ergs/cm² (table 3.15), i.e., a difference of 30ergs/cm². Similarly, the surface energy of the sample of series 1 with 200ppm diene is ~25 units higher compared to the one of series 2 with 200 ppm diene. Similar difference in magnitude of $\sigma_e$ is observed when they are calculated with a different set of parameter.

Another interesting fact to note is that unlike series 1, the difference in $\sigma_e$ values among the samples of series 2 is negligible and no systematic trend is observed with the diene content (there is only a slight decrease in the surface energy of the sample with 200ppm diene compared to the linear at all the different set of values of the parameters used). An uneven distribution of diene in the samples of series 2 might be responsible for the observed behavior, as it does not change the gamma content appreciably on addition of diene compared to samples of series 1.

The surface energy calculations were performed separately by assuming regime II and regime III in each case. The results led to the conclusion that the data for all the samples adheres to regime III rather than regime II, as the calculated values of $\sigma_e$'s assuming regime II were much higher (in a range of 200-400erg/cm²) compared to previous reported values and were discarded. The calculated values of the surface energies, using regime III, also lies (in higher extremes, with Tm₀=200°C) within the reported values in literature.

The secondary nucleation theory that has been used in this analysis was derived by Hoffmann to analyze the secondary nucleation or growth of crystals. Overall crystallization involves both primary and secondary nucleation; therefore, the analysis of overall nucleation using this theory may not always give the correct values of the crystal structure parameters. However, a very recent paper by Alamo et al.¹²⁹ modeled the temperature coefficient of the rate adequately with nucleation and growth theory, which may be more relevant to analyze the overall crystallization rate.

### 3.1.4.1.2 Temperature coefficient studies of linear growth rates

Following the analysis of overall crystallization rate, different set of parameters ($U^*$, $C_2$ and Tm₀) were used to obtain the interfacial surface free energies from analysis of the linear growth rate of the samples of series 1. The corresponding plots of $\ln(G) + U^*/R(T-T_\infty)$ against Tm₀/TcΔTf for series 1 are also shown in figure 3.59-3.62.
\begin{align*}
y &= -804.43x + 6.4606 \\
y &= -1139x + 13.37 \\
y &= -537.68x + 0.4903 \\
y &= -1004.8x + 10.525 \\
y &= -738.21x + 4.5368
\end{align*}

\begin{align*}
y &= -1004.8x + 10.525 \\
y &= -804.43x + 6.4606 \\
y &= -738.21x + 4.5368 \\
y &= -537.68x + 0.4903
\end{align*}

**Figure 3.59** Temperature coefficient analyses of linear growth rates of series 1 samples with $T_m^0=200°C$, $U^*=1500\text{cal/mole}$, $T_g=-15°C$, $C_2=30°C$, $T_{\text{inf}}=-45°C$

**Figure 3.60** Temperature coefficient analyses of linear growth rates of series 1 samples with $T_m^0=200°C$, $U^*=4120\text{cal/mole}$, $T_g=-15°C$, $C_2=51.6°C$, $T_{\text{inf}}=-66.6°C$
The temperature coefficient analysis (figure 3.59-3.60) of the growth rate data produced a transition from regime II to III for the linear and the sample containing 200 ppm diene, the transition temperatures are 139°C for linear and 141°C for the sample with 200 ppm diene, the small difference may be due to the change in molecular weight. The sample with 375 ppm diene did not exhibit any transition in the temperature range of 134-148°C. In agreement with previous interpretations the absence of break for the iPP with the highest amount of diene, LCB276K1.15, can be attributed to its high molar mass.

Table 3.16 Values of surface energy (linear growth) for series 1 samples obtained with $T_m^0=200°C$, Combined data for $U^*=1500\text{cal/mole}$ and $U^*=4120\text{cal/mole}$ (fig 3.59 and 3.60) ($\sigma_u=13.5\text{erg/cm}^2$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>$T_m^0$ (°C)</th>
<th>$U^* = 1500\text{cal/mole, C}<em>2=30°C$, $T</em>{inf} = -45°C$</th>
<th>$U^* = 4120\text{cal/mole, C}<em>2=51.6°C$, $T</em>{inf} = -66.6°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>$\sigma_s\sigma_e$ (erg/cm$^2$)</td>
<td>$\sigma_e$ (erg/cm$^2$)</td>
<td>Slope</td>
</tr>
<tr>
<td>IPP150K1.31</td>
<td>III</td>
<td>197.30</td>
<td>1139 1.42 1241 92 1261 1.42 1374 102</td>
<td></td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>III</td>
<td>197.55</td>
<td>1005 1.87 1095 81 1118 1.81 1218 90</td>
<td></td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>III (as)</td>
<td>197.6</td>
<td>738   1.60 1608 119 824 1796 133</td>
<td></td>
</tr>
</tbody>
</table>

The change in $T_m^0$ changed slightly the ratio of slopes of the two regimes for the two samples exhibiting transition, as seen in tables 3.16 and 3.17. However, changing the parameters of the transport term, at a fixed $T_m^0$, did not affect the ratio. Interestingly, the ratio of slopes for the sample with 200ppm of diene, HLIPP203K1.18 is in agreement with the theoretical value of 2 (with $T_m^0 = 459K$). The surface free energy of the sample containing 375 ppm diene was evaluated by assuming regime II and regime III separately. The values are listed in tables 3.16 and 3.17. In line with the previous analysis of overall rates, the surface energy values fall within the range of the previously reported values, the range is approximately between 50-150 ergs/cm$^2$, as detailed in previous section.
Figure 3.61 Temperature coefficient analyses of linear growth rates of series 1 samples with \( T_m^0 = 186^\circ C, U^* = 1500\text{cal/mole}, T_g = -15^\circ C, C_2 = 30^\circ C, T_{inf} = -45^\circ C \)

Figure 3.62 Temperature coefficient analyses of linear growth rates of series 1 samples with \( T_m^0 = 186^\circ C, U^* = 4120\text{cal/mole}, T_g = -15^\circ C, C_2 = 51.6^\circ C, T_{inf} = -66.6^\circ C \)
Table 3.17 Values of surface energy (linear growth) for series 1 samples obtained with $T_m^0 = 186^\circ C$, Combined data for $U^* = 1500$ cal/mole and $U^* = 4120$ cal/mole (fig 3.61 and 3.62) ($\sigma_u = 13.5$ erg/cm$^2$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>$T_m^0$$_{cop}$ ($^\circ C$)</th>
<th>$U^*$ = 1500 cal/mole, $C_2$= 30 $^\circ C$, $T_{inf}$ = -45 $^\circ C$</th>
<th>$U^*$ = 4120 cal/mole, $C_2$= 51.6 $^\circ C$, $T_{inf}$ = -66.6 $^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Ratio of slopes</td>
<td>$\sigma_u$/$\sigma_e$ (erg$^2$/cm$^4$)</td>
<td>$\sigma_e$ (erg/cm$^2$)</td>
</tr>
<tr>
<td>IPP150K1.31</td>
<td>III 183.40</td>
<td>682</td>
<td>1.54</td>
<td>743</td>
</tr>
<tr>
<td></td>
<td>II 183.40</td>
<td>442</td>
<td>2.63</td>
<td>444</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>III 183.62</td>
<td>592</td>
<td>2</td>
<td>637</td>
</tr>
<tr>
<td></td>
<td>II 183.62</td>
<td>293</td>
<td>1.38</td>
<td>445</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>III (as) 183.7</td>
<td>409</td>
<td>1.54</td>
<td>891</td>
</tr>
<tr>
<td></td>
<td>(as) 183.7</td>
<td>409</td>
<td>2.89</td>
<td>445</td>
</tr>
</tbody>
</table>

There is a steady decrease in $\sigma_e$ with diene content, for example, using a standard set of parameters, $T_m^0 = 186^\circ C$, $C_2 = 30^\circ C$, and $U^* = 1500$ cal/mol. Considering regime III the calculated value of the $\sigma_e$ for linear is 55 ergs/cm$^2$, that for the sample with 200 ppm diene is 47 ergs/cm$^2$ and the same for sample with 375 ppm is 33. Similar difference is observed with changing the set of parameters. Hence, the difference in $\sigma_e$ between the linear and the sample with maximum diene content is ~30±5 ergs/cm$^2$. A similar argument, as given previously for overall crystallization data, can be provided here regarding the decrease in surface energy with increase in diene content. The use of different set of parameters changed the absolute values of slope and surface energies, but the overall trend and transition temperatures were not affected.

Analysis of linear growth rate data of samples of series 2

The growth rates of the four samples of series 2 were analyzed using nucleation theory for different set of parameters (fig 3.63-3.66).
Figure 3.63 Temperature coefficient analyses of linear growth rates of series 2 samples with $T_m^0=200\,^\circ C$, $U^*=1500\,\text{cal/mole}$, $T_g=-15\,^\circ C$, $C_2=30\,^\circ C$, $T_{inf}=-45\,^\circ C$

Figure 3.64 Temperature coefficient analyses of linear growth rates of series 2 samples with $T_m^0=200\,^\circ C$, $U^*=4120\,\text{cal/mole}$, $T_g=-15\,^\circ C$, $C_2=51.6\,^\circ C$, $T_{inf}=-66.6\,^\circ C$
The analysis of growth rate data produced a break characteristic of regime II/III transition for the linear one and the sample with 50ppm diene at a Tc of 138°C. However, the growth rate data of the other two samples were analyzed between a Tc of 130-139°C, therefore they did not produced any break, and it may require to go higher Tc’s to observe the break.

Table 3.18 Values of surface energy (linear growth) for series 2 samples obtained with Tm$^0$=200°C, Combined data for U*=1500cal/mole and U*= 4120cal/mole (fig 3.63 and 3.64) ($\sigma_u = 13.5$erg/cm$^2$)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>Tm$^0_{cop}$ (°C)</th>
<th>U* = 1500cal/mole, C$<em>2$= 30°C, T$</em>{inf}$ = -45°C</th>
<th>U* = 4120cal/mole, C$<em>2$= 51.6°C, T$</em>{inf}$ = -66.6°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope</td>
<td>Ratio of slopes</td>
<td>Slope</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$)</td>
<td>$\sigma_e$ (erg/cm$^2$)</td>
<td>$\sigma_u \sigma_e$ (erg/cm$^4$)</td>
</tr>
<tr>
<td>IPP291K1</td>
<td>III 198</td>
<td>1148 1.2</td>
<td>1250 93</td>
<td>1237 1.12</td>
</tr>
<tr>
<td>II 198</td>
<td>961</td>
<td>2094 155</td>
<td>1099</td>
<td>2395 177</td>
</tr>
<tr>
<td>HLIPP275K1</td>
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<td>1235 1.69</td>
<td>1346 100</td>
<td>1356 1.64</td>
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<td>1594 118</td>
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<td>1796 133</td>
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<tr>
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<td>1033 1125 83</td>
<td>1178</td>
<td>1283 95</td>
</tr>
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<td>2250 167</td>
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<td>1117 1217 90</td>
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</tr>
<tr>
<td>II(as) 198</td>
<td>1117</td>
<td>2434 180</td>
<td>1232</td>
<td>2685 199</td>
</tr>
</tbody>
</table>

Figure 3.65 Temperature coefficient analyses of linear growth rates of series 2 samples with Tm$^0$=186°C, U*= 1500cal/mole, Tg = -15°C, C$_2$ = 30°C, T$_{inf}$ = -45°C
Figure 3.66 Temperature coefficient analysis of linear growth rates of series 2 samples with $T_m^0=186^\circ\text{C}$, $U^*=4120\text{cal/mole}$, $T_g=-15^\circ\text{C}$, $C_2=51.6^\circ\text{C}$, $T_{inf}=-66.6^\circ\text{C}$

The transition temperature agrees very well with previous literatures\textsuperscript{227, 229, 230}. However the ratios of slopes are lower in magnitude (table 3.18-3.19) compared to the theoretical value (especially for the linear sample). The data for the samples which did not produced the characteristic transitions were analyzed assuming both regime II and III separately for the different set of parameters used, but considering the previous results and the observed temperature for transitions, it can be suggested that the data for those two samples adheres to regime III behavior.

Similar to all above studies the change in $T_m^0$ from 200$^\circ\text{C}$ to 186$^\circ\text{C}$ did lowered the absolute values of surface energies but it did not have much effect on the transition temperatures as well as the ratio of slopes. Unlike of samples in series 1 the surface energy values lacked any systematic trend or behavior with the diene content for samples in series 2, similar reason as cited for the results of overall crystallization data of samples of series 2 can be applied here as well, i.e. a significant difference in polymorphic content between the linear and diene containing samples of series 1 is mainly responsible for the observed variation in surface free energy, whereas, the close proximity of the $\sigma_e$ values for the samples of series 2 is attributed to the
moderate difference between their polymorphic. However, a lower surface free energy does reflect more chain folding irregularities as suggested by Nair et al. The H-linked polymers have more irregularities in their chain compared to the linear ones, therefore the lowering of surface energy of these H-linked samples compared to their linear counterparts can also be attributed to its higher degree of chain fold irregularity.

3.19 Values of surface energy (linear growth) for series 2 samples obtained with \( T_{m0} = 186^\circ C \), Combined data for \( U^* = 1500\text{cal/mole} \) and \( U^* = 4120\text{cal/mole} \) (fig 3.65 and 3.66) \( (\sigma_u = 13.5\text{erg/cm}^2) \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>regime</th>
<th>( T_{m0_{cop}} ) (^{(\circ C)} )</th>
<th>( U^* = 1500\text{cal/mole}, C_2 = 30^\circ C ), ( T_{inf} = -45^\circ C )</th>
<th>( U^* = 4120\text{cal/mole}, C_2 = 51.6^\circ C ), ( T_{inf} = -66.6^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Slope</td>
<td>Ratio of slopes</td>
<td>( \sigma_u ) ( \text{erg/cm}^4 )</td>
</tr>
<tr>
<td>IPP291K1</td>
<td>III</td>
<td>184</td>
<td>665</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>184</td>
<td>563</td>
<td>1.18</td>
</tr>
<tr>
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<td>184</td>
<td>739</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
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<tr>
<td>HLIPP283K1</td>
<td>III (as)</td>
<td>184</td>
<td>612</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>II (as)</td>
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</tr>
<tr>
<td>HLIPP247K1</td>
<td>III (as)</td>
<td>184</td>
<td>662</td>
<td>1.8</td>
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<tr>
<td></td>
<td>II (as)</td>
<td>184</td>
<td>662</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The value of surface energies obtained lies within the range of reported values and the difference with the values of surface energies from series 1 growth rate analysis are much narrower compared to the difference observed on comparing the values obtained using overall crystallization rate data for the two series. For example, the \( \sigma_e \) values obtained from the analysis of growth rate data for the linear sample of both the series are identical when calculated using same set of parameters. Using \( T_{m0} = 186^\circ C \), \( C_2 = 30^\circ C \), and \( U^* = 1500\text{cal/mol} \), the calculated value of \( \sigma_e \) for the linear sample of series 1 was 55 ergs/cm\(^2\) and that of series 2 was 53.7 ergs/cm\(^2\). Using the same set of parameter the calculated value of \( \sigma_e \) for the sample with 200ppm of diene of series 1 was 47.7 ergs/cm\(^2\), and the one with 200ppm diene of series 2 was 53.4 ergs/cm\(^2\). Therefore from the analysis of growth rate data it can be concluded structural parameter of the sample of both the series is identical and they form similar type of chain folded crystals.
3.1.5 New theories regarding polymer crystallization mechanism

A semi-crystalline polymer is usually composed of lamellar crystallites which are separated by amorphous layers. Crystallization in polymer systems which transfers the entangled melt into a semi-crystalline state is a process of primary importance and has been studied since long time. Over the years various conceptual models have been proposed and worked out in order to study the mechanism and rate of polymer crystallization. One became dominant and is now widely used in the evaluation of data, that developed by Hoffman and Lauritzen\textsuperscript{213} (discussed in previous section). The model interprets an exponential law for the variation of the nucleation rate with the temperature that requires overcoming an activation barrier in order to place the first nucleating stem onto the growth face. A “Secondary nucleation” then presents the decisive step which determines the crystal growth rate. The growth rate of the lamellae represents a well-defined property that can be easily measured by optical microscopy. By the late 1980s Hoffmann Lauritzen model\textsuperscript{213} became very common to represent the temperature dependence of measured growth rates and for searching the predicted ‘regime transitions’in semicrystalline polymers.

In spite of considerable success The Hoffman–Lauritzen model was always confronted by criticism\textsuperscript{241, 242}, and in 1990’s a reconsideration began led by Ijima and Strobl\textsuperscript{243, 244}, triggered by new experimental observations. One of the major implications of Hoffmann-Lauritzen model was that the lamellar thickness is determined by the undercooling below the equilibrium melting point given by the Gibbs–Thomson equation (equation 3.37) apart from a minor correction which is necessary to provide a thermodynamic driving force.

\[ T_m(d_c) = T_m^0 - 2\sigma_e T_m^0/\Delta H_f d_c \]  

(3.37)

Here, \( T_m \) is the melting temperature of a crystallite with thickness \( d_c \), \( T_m^0 \) is the melting temperature of crystal with infinite thickness, \( \Delta H_f \) is the heat of fusion and \( \sigma_e \) is the specific free energy of the crystal-melt phase boundary.

Surprisingly, and hard to accept for many, a direct check of this relationship by time – and temperature dependent small angle X-ray scattering experiments by Strobl et. al. did not confirm this law\textsuperscript{245}. As it turned out, these authors concluded that the lamellar thickness is determined by the supercooling below another temperature, which is always located above the equilibrium melting point. In addition, the crystal thickness is not affected by the presence of co-units.
Early in the 1990s, Keller and his co-workers, carried out crystallization experiments on polyethylene at elevated pressures using a polarizing optical microscope\(^{246}\), and observed crystal formation via the hexagonal phase. Crystals nucleate into the hexagonal phase, then grow in size before they transform into the orthorhombic phase after a statistically initiated, second nucleation step. The authors interpreted their observations as a new example of Ostwald’s rule of stages\(^{247}\). This rule states that crystals always nucleate into a mesomorphic or disordered crystalline structure, which is the most stable one for nanometer-sized crystals. Because of differences in the surface free energy, this state may differ from the crystal modification which is macroscopically stable. With this rule as a clue Strobl et. al.\(^{248}\) developed a new model (shown schematically in figure 3.67) for polymer crystallization in order to interpret their observation\(^{245}\). The process starts with the attachment of chain sequences from the melt onto the lateral growth face of a layer with a mesomorphic structure of minimum thickness, which then spontaneously thickens. When a critical thickness is reached, the layer solidifies immediately by the formation of block-like crystallites. The last important step in crystal development is the stabilization of the crystallites in time, leading to a further decrease in the Gibbs free energy.

![Figure 3.67 Sketch of the route proposed for the formation of polymer crystallites by Strobl.](image)

(Adapted from Strobl, G; *Eur. Phys. J. E*, 2000, 3, 165)
In the above model two different crystalline states are present, native crystals and stabilized crystals. Therefore, two different crossing points are encountered (figure 3.68), $T_f^\infty$ (or $T_{zg}$) and $T_c^\infty$. Their positions control what happens during an isothermal crystallization followed by heating.

![Diagram](image)

**Figure 3.68** General form of inverse of crystal thickness ($d_c^{-1}$) vs temperature diagram of crystallizing polymers. A crystallization and a melting line crossing each other at a finite $d_c^{-1}$ (Source: Strobl, G; Eur. Phys. J. E, 2000, 3, 165)

At the point of entry chains are attached from the melt onto the lateral growth face of a mesomorphic layer with the minimum thickness. The latter is determined by the melt-mesomorphic (mesomorphic to amorphous) transition temperature $T_{zg}$. The layer spontaneously thickens until the second transition point $T_c^\infty$ is reached where native crystals form immediately.
(mesomorphic to crystalline). The subsequent stabilization transforms them into a lower surface free energy state.

Very recently (2007), Strobl applied his model to analyze the growth rate data of a linear polyethylene fraction\textsuperscript{249} and contradicted Hoffman’s interpretation, regarding the observation of regime transition with the same set of data. Hoffman obtained three linear ranges with application of his model to the growth rate of linear polyethylene fraction\textsuperscript{250}. The breaks at 129 and 121 °C are interpreted as I-II and II-III regime transitions, respectively.

Strobl opposed this, and checked the validity of Hoffman’s model. The equilibrium melting temperature of polyethylene (Tm\textsuperscript{0}) was taken by Strobl as ~145\textsuperscript{251}, the same taken by Hoffman. As mentioned earlier in this section, Strobl suggested from experimental evidence that the crystal thickness is not determined by the equillibrium temperature, but by another temperature located above Tm\textsuperscript{0} (referred as T_{zg}). In order to confirm his findings, Strobl extrapolated the growth rate data of Armistead and Hoffman\textsuperscript{250} to a temperature of zero growth rate (T_{zg}), and the extrapolation led to a value of 132.5°C, which is far removed from the Tm\textsuperscript{0}. However, he concluded that the accuracy of the data is insufficient for a reliable determination of T_{zg} (as there were only a few points at higher temperatures to obtain good extrapolation). Therefore, he carried out his own experiment on another polyethylene sample with data having higher accuracy, and surprisingly obtained the same T_{zg} of 132.5°C. Hence, according to Strobl, the growth rate of polyethylene is determined by the distance to T_{zg} 132.5 °C rather than the supercooling below Tm\textsuperscript{0} as is conventionally assumed.

Given the novel interpretation of Strobl to growth rate data, we tested his model on one of the isotactic polypropylene sample in order to obtain the T_{zg} for iPP. The equation used to test Strobl’s model was taken from one of his recent publication\textsuperscript{249}. The Turnbull Fisher equation was the initial equation (equation 3.32, shown earlier)

\[ G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_w)}\right) \exp\left(-\frac{K_g T_m^0}{T_c \Delta T_f}\right) \]

This equation can also be written as

\[ \ln \frac{G}{G_0} + \frac{U^*}{T_c} = -\frac{K_g}{T_{zg} - T_c} \]

\[ (3.38) \]

Tm\textsuperscript{0} is replaced by a variable temperature T_{zg}.
Differentiation of equation 3.38 followed by a reordering leads to the following equation

$$
\left( -\frac{d \ln(G / G_0)}{dT} + \frac{U^*}{T^2} \right)^{-1/2} = K_g^{-1/2} (T_{ZG} - T)
$$

(3.39)

The growth rate of the linear and 200ppm diene containing sample of series was plotted according to equation 3.39 to observe whether an extrapolation is possible to obtain the $T_{ZG}$. The results are shown in figure 3.69 (linear) and figure 3.70 (sample with 200ppm of diene).

Figure 3.69 Growth rate data of IPP150K1.31 plotted according to equation 3.39 to test validity of Strobl model. $U^*$ is taken as 1500cal/mol.

Figure 3.70 Growth rate data of HLIPP203K1.18 plotted according to equation 3.39 to test validity of Strobl model. $U^*$ is taken as 1500cal/mol.
From the above figures (3.69 and 3.70) it is observed that a linear extrapolation of the data was not possible to determine the zero growth rate temperature $T_{ZG}$. The variation of $\frac{d\ln G}{dT}$ against $T_c$ is almost constant, which prevents the data to follow a straight line and finally extrapolate in x axis. Therefore it can be concluded that Strobl’s analysis cannot be applied in the present study, and it can only be applied to those data where $\frac{d\ln G}{dT}$ decreases as a function of $T_c$.

3.1.6 Polymorphic behavior

3.1.6.1 Crystallographic forms in iPP

Isotactic polypropylene (iPP) presents complex polymorphic behavior. Three different crystalline forms ($\alpha$, $\beta$, and $\gamma$ forms) and a mesomorphic form have been described. All the polymorphic forms are characterized by chains in the stable 3-fold helical conformation. The polymorphic behavior is complicated by the presence of structural disorder in the crystalline forms. The four different polymorphic forms of isotactic poly(propylene) are outlined below:

The $\alpha$ or monoclinic form- The first structural characterization of alpha form was carried out by Natta and Corradini. They concluded that alpha form has a monoclinic unit cell (figure 3.71) with four three-fold helical chains. Subsequent analysis made it fairly clear that it may show various degrees of disorder in the positioning of the chains depending on thermal and mechanical history of the polymer. However, the unit cell dimensions and the ordered arrangement of three-fold right- and left-handed helices within the cell, as found for the first time by Natta and Corradini, remain substantially unchanged. This is the most common form obtained in poly(propylene) with high isotacticty, usually obtained on crystallization from melt.
Figure 3.71 Monoclinic unit cell. The parameters of monoclinic (alpha form) unit cell of polypropylene are: $a = 6.65$, $b = 20.96$ Å, $c = 6.5$ Å $\beta = 99^\circ 80$ (Lotz et. al. Polymer Vol. 37 No. 22, 4979, 1996)

The $\beta$ or hexagonal form- Commercial iPP, prepared with the traditional heterogeneous Ziegler-Natta catalytic systems, generally crystallizes in the stable $\alpha$ form\textsuperscript{79}. The $\beta$ and $\gamma$ forms may be obtained only under special conditions of crystallization. The $\beta$ form crystallizes only in the presence of nucleating agents\textsuperscript{256}. Elucidation of the structure of $\beta$ iPP has been a considerable challenge. From its discovery in 1989\textsuperscript{257}, it was clear that the structure had some form of hexagonal symmetry (figure 3.72). However, the diffraction pattern of single crystals displays a number of reflections that require a large unit-cell. Because of its exceptionally low nucleation frequency as compared to $\alpha$-iPP\textsuperscript{258}, it coexists with nonnegligible amounts of $\alpha$-iPP. Considerable obstacles in the structural characterization of $\beta$-iPP are thus the simultaneous presence of other crystalline phases\textsuperscript{259} and of disorder. The structure was finally solved in 1994, independently by Meille\textsuperscript{256} and Lotz\textsuperscript{260}. Both teams reached the same structural solution: a trigonal cell containing three isochiral helices.

Figure 3.72 Hexagonal unit cell. The parameters of hexagonal (beta form) unit cell of polypropylene are, $a = b = 19$ Å, $c = 6.5$ Å (Lotz et. al. Polymer Vol. 37 No. 22, 4979, 1996)
The γ or orthorhombic form- Gamma crystals are characterized by a nonparallel arrangement of the chains within the unit cell. The gamma phase was initially indexed as triclinic, subsequently, studies of a form generated at atmospheric pressure from low molecular weight polymer led to a reassignment of the structure as orthorhombic (figure 3.73) with a unique crossed arrangement of the chains in subsequent growth layers. γ-iPP was considered a rare crystalline form of iPP until the discovery of the new homogeneous initiating systems, since with conventional heterogeneous Ziegler-Natta catalyst systems the γ form was obtained only under special conditions, i.e., by crystallization from the melt at elevated pressures (5000 atm), or by crystallization at atmospheric pressure of low molecular weight samples. Studies have reported that the presence of alpha phase is necessary for the branching and growth of gamma phase.

Figure 3.73 Orthorhombic unit cells. The parameters of orthorhombic (gamma form) unit cell of polypropylene are: a = 8.54 Å, b = 9.93 Å, c = 42.41 Å (Lotz et. al. Polymer Vol. 37 No. 22, 4979, 1996)

WAXD is usually used as a fingerprint to detect the presence of the different polymorphic forms in iPP, as shown in Figure 3.74. The diffractions characteristic and the corresponding 2θ value of each polymorph are indicated by, arrows.
Mesomorphic form- The presence of a mesomorphic form was first reported by Slichter and Mandell\(^\text{266}\). Subsequently, Natta\(^\text{267}\) pointed out the existence of a form of iPP having a degree of order intermediate between crystalline and amorphous phases. This material was obtained by quenching thin sheets of iPP from the melt in ice water. Its X-ray spectrum was similar to that reported by Slichter and Mandell\(^\text{266}\). This form was later termed as “mesomorphic form”. The transformation of the mesomorphic form into $\alpha$ form by annealing at temperatures higher than 70°C was also reported by Natta\(^\text{267}\). On the basis of IR spectra Natta and co-workers recognized that in this partially ordered phase the individual chains of iPP maintain, for a large fraction of their length, the three-fold helical conformation as in crystalline iPP. They concluded that this modification contains bundles of parallel stretches of right- and left-handed three-fold helices in which less order is present in the plane perpendicular to the chain axes than in the direction parallel to them.
3.1.6.2 Kinetic and thermodynamic requirements to form α and γ phases

The packing energy calculation shows gamma as a thermodynamically\textsuperscript{268} more stable form than the alpha, whereas alpha is more favored kinetically. Alamo et al demonstrated\textsuperscript{83} that at the very initial stages of crystallization (isothermal) the rate of formation of both polymorphs are the same but at intermediate and later stages of crystallization the rate of formation of the polymorphs depend on the overall defect content of the sample and the chosen crystallization temperature.

The variation of gamma form with isothermal crystallization temperature was studied separately for isotactic polypropylenes homopolymers with varied contents of defects\textsuperscript{269,270} and for propylene copolymers\textsuperscript{171, 271}. From these studies it was concluded that random distribution of defects or short isotactic sequences are the main factors responsible for the formation of gamma polymorph. Researchers observed a local maxima in the content of gamma form with temperature for polypropylene homopolymers or low defect content propylene-ethylene copolymers (1.8 mol% defect), but for copolymers like propylene-hexene (with 2 mol% defect) or any other copolymers, they did not observe the local maxima with temperature because of long crystallization kinetics at higher temperatures and the depletion of long crystallizable sequences that form the alpha phase. The presence of maxima in the content of gamma form with temperature is attributed to the fact that the concentration of crystallizable sequences, i.e., those of length that equal or exceed the requirement for a nucleus of critical size, changes with temperature. The following plot taken from a publication by Alamo et. al.\textsuperscript{83}, demonstrates the observation of maxima in the gamma content as a function of $T_c$ for various metallocene iPP’s and one Ziegler (Z 1.26), the values in the parenthesis corresponding to each curve denotes the overall defect content for each of the samples.
It has been demonstrated\(^\text{83}\) that at lower temperatures the critical number of repeating units required in a chain direction to form a crystal (\(\varepsilon^*\)) is small, and such a small lower limit for \(\varepsilon^*\) allows the smaller sequences to crystallize in extended form and the larger ones crystallize by folding. As a result at higher undercoolings the availability of long noncrystallizable sequences attached with the portion of crystallizable segment, which are essential for the formation of gamma phase, are low and only alpha type crystals will be observed. However, as the undercooling is lowered, the \(\varepsilon^*\) increases and very short sequences can no longer crystallize. In the remaining group of crystallizable sequences the shorter ones can still not crystallize by folding because the associated noncrystallizable sequences have become too long. Thus, in order for a lamellar crystallite to evolve in extended form, from this sequence, tilting and gamma formation will occur. Further increase in the crystallization temperature reduces the availability of shorter sequence continuously, and at sufficiently high temperatures, above the maximum, only a small amount, if any, of gamma will form due to the higher requirement. At lower temperatures...
undercoolings, the noncrystallizability of the shorter sequences that are required will prevent the formation of gamma phase. Since the alpha form only crystallizes from the longer sequences and the lamellar crystallites are propagated by some type of chain folding, they will dominate at the higher crystallization temperature.

Isotactic polypropylene crystallizing in a mixture of α and γ form usually exhibits two melting peaks, the lower melting is associated with γ and the higher one with α. From the DSC melting peaks and WAXS studies it was proven that the gamma form melts at a lower temperature than the parent alpha form which suggests that the gamma form has thinner crystallites.

In the present study, the simultaneous isothermal development of alpha and gamma phases in the two series of iPP can be followed by monitoring the overall crystallization rate in DSC or by WAXS. A quantitative kinetic analysis of the polymorphic contents was done by monitoring the development of endothermic peaks of each of the polymorphs at a fixed isothermal crystallization temperature as a function of time and converting them to heat of fusion in order to get the polymorphic contents. The results of the kinetic studies can be implemented to study the morphology and can predict whether the growth rate of pure gamma polymorph can be isolated at any isothermal crystallization temperature once the alpha polymorph levels off and stops growing.

Owing to the difference in defect distribution caused by specific catalyst system, i.e. for metallocene catalyst the intramolecular distribution of defects is random, whereas for Ziegler Natta the intramolecular defect distribution is blocky, isotactic polypropylene prepared with homogenous metallocene catalysts crystallize in the gamma form more easily than those prepared with heterogenous Ziegler-Natta catalyst, not requiring high pressure. A major consequence of applying hydrostatic pressure is that it enables the crystallization to be conducted at higher temperatures. Thus, higher γ concentrations are expected relative to those obtained at atmospheric pressure. Alamo. et. al. demonstrated that isotactic polypropylene with overall defect content as low as 0.41mol% exhibited measurable gamma contents when crystallized at relatively high temperatures. The effect of molecular weight on the gamma content was also studied in that report and it was observed that no definitive trend in the γ content could be discerned with molecular weight. However, De Rosa et. al. observed at same concentration of stereo and regio defects (for iPP) the amount of γ form crystallized is independent of the
molecular mass in the range of 200,000-600,000, whereas with decreasing the molecular mass below 100,000 the amount of \( \gamma \) form decreases and the crystallization of the \( \alpha \) form is favored. De Rosa related this observation to the presence of more concentration of regio defects in the higher molecular weight samples.

The polymorphic content of the H-linked samples with the linear one was compared under identical crystallization condition in the present study in order to investigate the effect of additional linkage (or defects) on the polymorphic forms. Owing to the fact that the overall defect content of the samples is very similar, the major factor influencing the polymorphic behavior will be the effect of branch points. The study of the samples of series 2 allowed us to analyze the effect of H-linkages exclusively (since molecular weight and overall defect contents are constant) on the polymorphic behavior.

3.1.6.3 Analysis of polymorphic content

The samples of series 1 and 2 were isothermally crystallized at different temperatures to cover a wide range in content of gamma phase. The corresponding WAXD and DSC thermograms for the three samples of series 1 at different Tc’s are shown in figure 3.70 and 3.71 respectively. The variation of gamma content with Tc is clearly evident from the plots shown in Fig. 3.76 a-c for series 1. Following the intensity of the characteristic \( \gamma \) peak at 20.8° in the diffractograms, we see that this diffraction is absent at 100°C, increases with increasing Tc up to ~130°C, and then decreases with further increase of Tc. WAXD shows that after isothermal crystallization from melt a maximum in the gamma content is reached at ~130°C, following the trend exhibited by other iPP homopolymers\(^8^3\). Support for the existence of the maxima is also found in the corresponding melting behavior, shown in Fig 3.77 a-c for the same set. The fractional content of gamma form, evaluated from the heat of fusion of the lower melting peak, reached its maxima a 130°C and starts decreasing thereafter. The position of maxima (Tc = 130°C) does not seem to vary with addition of diene or molecular weight.
Figure 3.76 WAXS Diffractograms of samples of Series 1, At Tc’s a) 100°C, b) 130°C and c) 145°C
Figure 3.77 DSC Thermograms of samples of Series 1, at Tc’s a) 100°C, b) 130°C and c) 145°C
There are different ways to evaluate the content of gamma phase from WAXD diffractograms. These methods are not equivalent; hence, it is important to quantify the content of gamma phase using the same criterion.

The earliest method was described by Turner Jones, detailed in the experimental section. A second method is to compute heights using the WAXD baseline (shown in figure 3.78).

![WAXD diffractogram](image)

**Figure 3.78** The WAXD diffractogram of HLIPP203K1.18 at 130°C is shown. The fractional content of gamma phase was obtained from the ratio of the heights, \( H_\gamma / (H_\gamma + H_\alpha) \). The heights were measured from the base of the diffractogram.

In this method the gamma content is also obtained from the ratio of heights of the peak, similar to Turner Jones. The only difference being that unlike Turner Jones method, the baseline method (figure 3.78) computes the peak height from the base of the diffractogram. The gamma content for the three samples of series 1 computed using baseline method is plotted in figure 3.79 and that computed using Turner Jones method is plotted in figure 3.80.
Figure 3.79 Gamma content of the three samples of series 1 as a function of Tc obtained using the baseline method from WAXS. Continuous lines are drawn manually to guide the eye over trends of data.

Figure 3.80 Gamma content (from WAXS) as a function of Tc, for samples of Series 1, obtained by Turner Jones method. Continuous lines are drawn manually to guide the eye over trends of data.

As seen from figure 3.79 and 3.80 the difference in values obtained for %gamma from the two methods is very not very significant at a fixed Tc. Therefore, it may be concluded that in the range of gamma developed by the samples for the present study, the two methods lead to the same results.
Figure 3.81 Gamma content (from WAXS) as a function of Tc, for samples of Series 2, obtained by Turner Jones method. Continuous lines are drawn manually to guide the eye over trends of data.

The gamma content at each Tc for series 2 as obtained from Turner Jones\textsuperscript{98} method is plotted in figure 3.81. Under identical crystallization conditions, the gamma content depends directly on the total defect content of the sample studied. In series 1 we have three different samples with the total defect content ranging from 1.15-1.31, accordingly not much difference in the polymorphic content is expected.\textsuperscript{83} However, it was observed that the gamma content of the two diene containing samples is higher throughout the temperature range studied when compared to linear one. The H linked iPPs exhibit \textasciitilde15\% higher gamma content compared to the linear one for all isothermal crystallization temperatures. This higher gamma content can be attributed to the presence of diene, since the diene produces “H” branching that contributes to the total defects in addition to the overall stereo and regio defects listed. As observed by Alamo et. al.,\textsuperscript{83} for linear metallocene iPP’s the difference in defect content needs to be at least 0.6-0.7mol\% in order to exhibit \textasciitilde20\% difference in gamma content. Therefore, in the present study it can be assumed that the observed increase in gamma content parallels the reduction of the average isotactic sequence length due to the presence of additional irregularities introduced by the H-links. It appears that the H linkages enhances the development of the gamma phase.
In the samples of series 2 the gamma form also seems to increase with addition of diene, though the difference in gamma content with diene is much moderate compared to series 1. The difference in gamma content between the two linear iPP of series 1 and 2 is minimal (~5%) owing to close proximity of their total defect content (1.31 vs 1 mol%). However, the increase in the gamma content by addition of equivalent amount of diene to the samples of series 1 is significant as compared to series 2 (figure 3.82). The gamma content of the sample in series 1 containing 200 ppm of diene is almost 10-15% higher than the linear at all the Tc's measured whereas the difference in gamma content of the 200 ppm and linear in series 2 is around 5-7%. Therefore, it can be concluded that although the addition of diene (H-links) invariably increases the content of gamma form, however the magnitude of increase depends on the distribution of the branches. This difference is attributed to the uneven distribution of the LCB in the copolymer molecules of series 2. As was shown in other works, the content of gamma phase is very sensitive and inversely proportional to the average isotactic sequence length ($n_{iso}$)\textsuperscript{272, 83}. In the present study, compared to the random LCB distribution of series 1, the average isotactic sequence length in the copolymers of series 2 increases due to the preferential concentration of LCB in the shorter chains, hence, a comparatively lower content of gamma phase is expected (and found) in this series.

![Graph showing gamma content as a function of Tc for samples with 200 ppm diene of each series.](image)

**Figure 3.82** Gamma content as a function of Tc for samples with 200 ppm diene of each series. The difference in enhancement of gamma content on addition of 200 ppm diene to the linear samples of the two series having almost equivalent amount of gamma form is highlighted.
3.1.6.4 Gamma content of nucleated iPP

The effect of nucleation on the gamma content can be analyzed by comparing the gamma content of the externally nucleated specimens compared to the non nucleated one under similar crystallization conditions. The optical micrograph images for the samples of series 1 led to the conclusion that the H-linked or diene containing samples have considerably higher nucleation densities compared to the linear one at a fixed crystallization temperature. To test if this increase in nucleation could be correlated with the increase in the fraction of gamma crystals, a 0.25 % nucleating agent (Millad 3988(3,4-dimethyl dibenzylidene sorbitol) was added to the linear and H-linked iPPs of the samples of series 1. The polymorphic behavior of nucleated and non-nucleated iPPs was compared.

The gamma content of the externally nucleated species of all the three samples of series 1 is compared with their non nucleated counterpart in the same range of Tc in figure 3.83 (a, b and c). The gamma content is basically equivalent for nucleated and non-nucleated samples (series 1). This result rules out any correlation between nucleation density and the enhanced content of gamma phase observed in H linked iPPs.

![Figure 3.83](image)

Figure 3.83 Gamma content comparisons of nucleated and non nucleated samples of Series 1 (a) 0 ppm, (b) 200 ppm and (c) 375 ppm. Note the negligible difference observed in the gamma content of the nucleated and non nucleated specimen in each figure. Continuous lines are drawn manually to guide the eye over trends of data.
**Figure 3.83** – continued

![Gamma content comparison of nucleated and non nucleated samples of Series 1 (a) 0 ppm, (b) 200 ppm and (c) 375 ppm. Note the negligible difference observed in the gamma content of the nucleated and non nucleated specimen in each figure. Continuous lines are drawn manually to guide the eye over trends of data.](image)

3.1.6.5 **Kinetic development of α and γ phase**

The enthalpy of fusion of the two polymorphs is obtained by deconvolution of the DSC melting peaks, specific to the respective polymorph, after crystallizing the iPP samples isothermally at a fixed Tc as a function of time. The evolution with time of the heat of fusion corresponding to each polymorph is shown for selected crystallization temperatures (Tc) for the three samples of series 1 in Figures 3.84 (a-c). These figures give quantitative data of the α and γ
crystallinities developed with time during isothermal crystallization. In all the samples, at any 
Tc, both polymorphs are formed simultaneously from the early stages of the crystallization and 
both evolve with the typical sigmoidal behavior. Furthermore, it is observed that both 
polymorphs level off after the same time at all the crystallization temperature studied. This result 
can be interpreted from the WAXS data considering the final relative content of gamma form 
that the samples develop. From analysis of WAXS data it was observed (figure 3.80) that 
between 120 and 140°C all the samples of series 1 have a final gamma content between 40-60%, 
as a result we expect both polymorphs to level off almost at same time at any crystallization 
temperature chosen between this range, which is evident in the figure.

Figure 3.84 Development of α and gamma phase with time for samples of series at indicated 
Tc’s, IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15. Open symbols represent 
gamma phase and closed ones represent alpha phase.
Figure 3.84 Development of $\alpha$ and gamma phase with time for samples of series at indicated Tc's, IPP150K1.31, (b) HLIPP203K1.18 and (c) HLIPP276K1.15. Open symbols represent gamma phase and closed ones represent alpha phase.
Recently, similar experiments were carried out in our laboratory with propylene ethylene copolymers with mol% ethylene varying from 0.8–4.6%, and total defect ranging from 1.6–5.8%. An example of the crystallization kinetics studied in that paper monitoring the growth of two polymorph (sample with 5.8 mol% defect) as a function of time is given in figure 3.85. The evolution of the heat of fusion shown in the figure indicates that at any of the experimentally accessible Tcs, there is an interval of time for which crystallization proceeds exclusively via the formation and growth of \(\gamma\) crystallites, the region where \(\alpha\) levels off and \(\gamma\) continuous to grow. Thus, figure 3.85 enable time frames in the crystallization process to isolate the behavior of the \(\gamma\) phase from the crystallization of mixed \(\alpha + \gamma\) phases. Thus, in that paper it was possible to study the growth rate of pure gamma form by extending the measurements of the spherulitic radius with time to the region where pure gamma form prevails. The difference in growth rate of the pure gamma form compared to the mixed form is documented and it was concluded that linear growth rates for pure \(\gamma\) phase are significantly lower than those that correspond to mixed \(\alpha + \gamma\) development.

![Figure 3.85](figure.png)

**Figure 3.85** Sigmoidal development of \(\alpha\) (filled symbols) and \(\gamma\) (open symbols) crystallinities with time for a propylene ethylene copolymer with 5.8 mol% total defects, at the indicated temperatures (Adapted from, Alamo, et al. *Macromolecules*, 2003, 36, 5623)
In the present study, it is not possible to isolate the growth of pure gamma form in the range of accessible crystallization temperatures (Tc), as is evident from figure 3.84. Only for certain Tcs a difference in the temporal evolution of the two forms is observed, for example considering HLIPP276K1.15 at 138 °C in figure 3.84c, it is observed that growth of gamma phase levels off after a certain time and that of alpha phase increases with time. As a consequence, the kinetic study has to be carried out above 140°C in order to observe the growth of pure alpha phase, but under no circumstances we would be able to monitor the growth of pure gamma because the final relative content of gamma does not exceed 55-60% for all of the samples at any isothermal crystallization temperature (Tc).

In order to study the morphology and growth of pure gamma phase in a range of Tc similar to this study, an iPP sample with higher overall defect content would be required, thus leading to higher overall gamma content. This has been evidenced by Alamo et al.\textsuperscript{83} in their work on metallocene iPP homopolymers. In that study it was observed that for an iPP with 2.35mol% defects, the maximum in gamma content reaches a value of 80% at 120°C. As shown in figure 3.86, the kinetic studies in the entire range of Tc (~120°C) suggested that growth of pure gamma form could be isolated from the mixed polymorphic growth.

\textbf{Figure 3.86} Sigmoidal variation of the development of $\alpha$ and $\gamma$crystallinities, $(1 - \lambda)$, with time for sample M335K2.35 crystallized at the following temperatures: (o, •) 117 °C, (∇, ▼) 124.5 °C, (□, ■) 129 °C, (∇, ▼) 133 °C, (o, •) 138 °C. Open symbols, $\gamma$crystallinity; closed symbols, $\alpha$ crystallinity. (Adapted from, Alamo, et al. \textit{Macromolecules}, 1999, 32, 12, 4050)
3.1.7 Rheology

The knowledge and the design of flow behavior are essential for thermoplastic polymers, since all forms of production and processing occur in the molten state. Entangled polymer melts can display a wide range of rheological behaviors depending on the molecular architecture.

The relation between melt viscosity and molecular weight of entangled linear polymers can be described with considerable accuracy by a power law (equation 3.40):\[ \eta_0 \propto M^{3.4}, \quad M > M_c \] \hfill (3.40)

The molecular weight $M_c$ is a characteristic constant of the species in the melt state. Typically, $M_c \sim 2M_e$, where $M_e$ is the entanglement molecular weight.

The origin of the above form traces back to 1951, when Fox and Flory, from theoretical derivation, related intrinsic viscosity of the polymer with molecular weight ($\eta M \propto R^3$) on the basis of measurements on narrow distribution fractions of polystyrene and polyisobutylene. The relation has since been shown to apply to both melts and concentrated solutions for many species of flexible polymers.

Addition of branches to linear polymers significantly influences the flow behavior. Some quite striking differences from linear polymer behavior are found, especially when entanglement interactions are important. The molecular mass dependence of zero shear-rate viscosity of long-chain branched polyethylenes was explained in detail by Janzen and Colby. The Number and length of the branches are two important parameters influencing the flow behavior. The authors concluded that the molecular mass between branch points is decisive for the viscosity behavior of long-chain branched polyethylenes. An increase in zero shear-rate viscosity is found in the case where the molecular mass between branch points is much larger than the entanglement molecular mass. Whereas, for a high branching density the molecular mass between branch points becomes small and therefore leads to a reduced zero shear-rate viscosity (reduction of the hydrodynamic radius by long-chain branching is responsible for a decrease in zero shear-rate viscosity) in comparison to linear polyethylene.

Theoretical work and experimental data demonstrate that the molecular mass dependence of zero shear viscosity of well-defined model long-chain branched polymers follows an exponential behaviour. Mcleish et. al were able to explain, for instance, the empirically found exponential dependence of the zero shear viscosity ($\eta_0$) for LCB polymers on the ratio of $M_a/M_e$: \[ \eta_0 \propto M_a^{3.4}, \quad M_a > M_c \] \hfill (3.40)
\[ \eta_0 \propto (M_a/M_e)^\alpha \exp(\nu M_a/M_e) \]  

The molar mass \( M_e \) of a strand between two entanglements is a characteristic parameter of a polymer, \( M_a \) describes the molar mass of the long-chain branch, and \( \alpha \) and \( \nu \) are constants of the order of 1 and 0.5, respectively.

Such type of behaviour has been reported for star polymers of polystyrene\textsuperscript{280} and polyisoprene\textsuperscript{281}. Lohse et al.\textsuperscript{282} reported an increase in zero shear viscosity above the linear benchmark from analysis of the melt shear rheology for well-defined model long-chain branched polyethylenes (symmetric, asymmetric stars) containing multiple branched chains (all of them have a local structure identical to an LLDPE with 7-10 wt % butene i.e., two to three ethyl branches per 100 backbone carbons). Lohse, et.al. defined the backbone of star polymers to be the sum of the lengths of the longest two arms. They observed that star polymers tend to have much higher \( \eta_0 \) than linear polymers of similar molecular weight. It has long been observed that \( \eta_0 \) for symmetric stars do not depend on the total molecular weight, or on the functionality of the stars, but rather exponentially on the arm molecular weight, \( M_{arm} \textsuperscript{283} \). This is in marked contrast to the power-law dependence on molecular weight seen for linear polymers. This occurs because the stress relaxation of stars is controlled by arm retraction, rather than chain reptation, as in the case of linear polymers. Assymetric star polymers were made so that the effective backbone (that is, the sum of the lengths of the two longest arms) had similar \( M_w \) (~100kg/mol) compared to linear ones. Molecular weight of the “branch” (the shortest arm) varied from 5 to 50 kg/mol. In most cases, this was placed in the center of the backbone (central branch). For the asymmetric star molecules, the zero shear viscosity increases monotonically as the length of the central branch rises.

Lohse et. al.\textsuperscript{282} concluded that long chain branched molecules had broader relaxation spectra and longer relaxation times in comparison to a linear molecule. This causes more resistance for the backbone to relax and raises the zero shear viscosity compared to their linear counterpart. Zhu, et. al.\textsuperscript{284} studied a series of LCB PE synthesized using Dow Chemical CGC-Ti catalyst system, having approximately the same \( M_w \) and narrow MWD. The LCB densities were in the range of 0~0.44 branch per 10,000 carbons. It was observed that such low LCB density levels resulted in an increase of both zero shear viscosity and shear thinning. Rheological property of LCB-PE produced by copolymerization with nonconjugated \( \alpha, \omega \) diene was studied\textsuperscript{285} subsequently, and it was observed that with increase in diene content both the zero
shear viscosity and Mw increases in parallel (an addition of 2.9mol% of 1,5 hexadiene to linear polyethylene increased the Mw from 77 to 113kg/mol and $\eta_0$ from 1300 to 5100 Pas).

Polydispersity is another parameter that may influence the zero shear-rate viscosity. However, influence of polydispersity is judged contradictorily in the literature. For linear polyethylenes, both Kazatchkov et al.\textsuperscript{286} and Wasserman\textsuperscript{287} report a significant influence of polydispersity on the zero shear-rate viscosity. Both papers state that the viscosity increases with increasing polydispersity. Kazatchkov observed a systematic increase of the zero shear viscosity with increase in polydispersity index (PI), keeping the Mw fixed at ~100kg/mol ($\eta_0$ increased from 14.22 to 37.42kPas on increasing the PI from 3.3 to 12.7). On the other hand, at almost fixed PI (between 3 and 4) for LCB polypropylenes (LCB introduced by electron beam irradiation), Munstedt et. al.\textsuperscript{288} observed that that $\eta_0$ increased from 3.7 to 188kPas at 180°C on increasing the Mw from 268 to 669 kg.mol. In the same publication\textsuperscript{288}, for a set of HDPE’s, they observed a zero shear viscosity –weight average molecular mass relationship of linear polyethylenes, which is clearly independent of polydispersity. The zero shear viscosity of the HDPE increased from 0.1 to $2.61 \times 10^7$ Pas at 150°C on increasing the Mw from 5 to 1000 kg/mol, with polydispersities between 1.4 and 8. This finding (by Munstedt on the LCB polypropylenes) supports earlier publications of Masuda\textsuperscript{289} et al. on polystyrenes and their blends, where at a fixed PI (~1) the zero shear viscosity increased steadily with increase in Mw from 300, 000 to 600,000 g/mol. From the above studies it can therefore be concluded that the zero shear viscosity actually depends (increases) mainly on the addition of chains to higher molecular weight region rather than on the numerical value of PI.

Much less research has been carried out on the extensional properties of LCB PP melts because appropriate samples (as peroxide grafting or electron beam irradiation invariably influenced molecular weight and sometime form crosslinks in addition to introducing LCB) have been difficult to obtain. In the past decade, many researchers have investigated LCB polyolefin by rheological method, but most studies focus on PE or model polymers and only a few reports are available regarding LCB PP, as LCB PP is difficult to obtain and the degree of LCB is very low\textsuperscript{290,292}. When PP is modified by peroxide and polyfunctional monomer, the reaction and the product components become very complex. Degradation reaction makes the molecular weight to decrease, grafting reaction introduces short chain branch (SCB) structure, branching reaction introduces LCB structure, and gel will be produced if crosslinking reaction can happen. The
complex reactions as well as the complex products make the investigation on LCB PP very difficult.

An example of the above complexities produced during synthesis of peroxide modified PP’s were demonstrated by Tian et. al.\textsuperscript{291}. This will provide a better understanding of the effect of LCB produced by peroxide addition to linear polypropylene on the rheological properties. In this paper LCB PP’s were prepared by melt grafting reaction in the presence of 2,5-dimethyl-2,5(tertbutylperoxy) hexane peroxide and pentaerythritol triacrylate (PETA), and they were characterized by rheological methods. The characteristics of these samples are listed in Table 3.20.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Sample & Grafting degree (wt\%) & $\eta_0 (\times 10^4 \text{Pas})$ \\
\hline
PP & - & 2.00 \\
D0 & - & 0.88 \\
D1 & 0.13 & 1.85 \\
D2 & 0.18 & 1.92 \\
D3 & 0.26 & 2.74 \\
D4 & 0.30 & 3.62 \\
D5 & 0.55 & 4.57 \\
\hline
\end{tabular}
\caption{Rheological parameters of the plain PP and modified PPs, (D, designates the modified PP, D0 refers to the sample when only peroxide was used and D1-D5 refers to the samples where PETA was added with the peroxides, Source: Tian et al. Polymer, 2006, 47, 7962)}
\end{table}

The complex viscosity curves are of interest in reference to our iPP studies, they are hence reproduced in Figure 3.87 below.
From the figure it is evident that when only peroxide was used (sample D0), the complex viscosity decreased rapidly at low frequency, indicating that there was only degradation reaction and the molecular weight decreased. With the addition of PETA, the complex viscosity curves became higher than that of D0 at low frequency, indicating that the additions of PETA reduced the degradation. Further, the viscosity of PP at low frequency increased gradually when more PETA was used. The complex viscosity of modified PP’s were higher than that of the plain PP at low frequency, while at high frequency modified PP’s exhibited higher shear thinning than the linear. This is the typical behavior of polymers with long chain branching\footnote{Error! Bookmark not defined.}. Therefore, a similar behavior is expected for the set of LCB samples used for the present study.

In 2004, Gotsis et. al.\textsuperscript{292} synthesized long chain branched polypropylenes using a myristyl-peroxydicarbonate P-26. The molecular characteristics are given in table 3.21.
Table 3.21 Molecular characteristics of a polypropylene (B, 0 mmol of P=26) modified using varying amounts (mmol/100 g PP) of P-26 (dimyristyl peroxydicarbonate, Source: Gotsis et al. J. Rheol, 2004, 48, 895).

<table>
<thead>
<tr>
<th>P-26 (mmol)</th>
<th>Bn*</th>
<th>Mw ×1000</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>422</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
<td>575</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
<td>574</td>
<td>7.6</td>
</tr>
<tr>
<td>3</td>
<td>0.7</td>
<td>581</td>
<td>8.6</td>
</tr>
</tbody>
</table>

*BBranches per molecule (Measured using High temperature SEC)

The weight average molecular weight (Mw) does not change much with increase in level of branching, but zero shear viscosity (η₀) increased in parallel with LCB (figure 3.88). Similar result was obtained for long chain branched PE by Janzen et. al. 11

Figure 3.88 Dynamic shear viscosity vs the frequency at 190 °C for the melts of linear PP, designated as B (0 mmol of P-26, listed in table 29) and its modification with P-26. (Source: Gotsis et al. J. Rheol, 2004, 48, 895)
Copolymerization of polypropylene with non conjugated dienes produces LCB polypropylene with simpler structures than the LCB produced by grafting or electron beam. The rheological characterization of metallocene catalyzed LCB polypropylene (LCB introduced by copolymerization with 1,9 decadiene) was carried out in a recent paper. It was observed that 1,9-decadiene had a great influence on molar masses. Even small amounts (0.6 mol%) of comonomer (1, 9 decadiene) raised molar mass of the homopolymer from 180 to 544 kg/mol. Zero shear viscosities of the measured samples were extrapolated from the complex viscosity curves. Zero shear viscosity was observed to depend mainly on the molar mass. The polypropylene copolymers gave much higher zero shear viscosity than would have been expected based on the molar masses (summarized in table 3.22). One obvious reason could be the much broader molar mass distributions as was evident from GPC measurements. Zero shear viscosity is also greatly affected by a high molar mass tail as well as long-chain branching or crosslinkage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comonomer (mol %)</th>
<th>Mw (kg/mol)</th>
<th>Mw/Mn</th>
<th>Extrapolated η₀ at 200°C (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymer</td>
<td>0</td>
<td>180</td>
<td>2.4</td>
<td>892</td>
</tr>
<tr>
<td>Copolymer 1</td>
<td>0.40</td>
<td>368</td>
<td>4.8</td>
<td>39798</td>
</tr>
<tr>
<td>Copolymer 2</td>
<td>0.64</td>
<td>544</td>
<td>9.1</td>
<td>80709</td>
</tr>
</tbody>
</table>

Rheological study of metallocene catalyzed LCB iPP with 1,9 decadiene has been performed by Zhu et al. The molecular characterization of those samples is given in table 3.23.
Table 3.23 Molecular characterization of the samples. PP1 is the homopolymer. PP2-PP4 are the copolymers with increasing amount of 1,9 decadiene. (Source: Ye et al. Ind. Eng. Chem. Res. 2004, 43, 2860)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene conc (mmol/L)</th>
<th>Mn (kg/mol)</th>
<th>Mw (kg/mol)</th>
<th>Mw/Mn</th>
<th>LCBD (per 1000 C)</th>
<th>Extrapolated η₀ at 190°C (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP1</td>
<td>0</td>
<td>91.4</td>
<td>224.6</td>
<td>2.5</td>
<td>0</td>
<td>900</td>
</tr>
<tr>
<td>PP2</td>
<td>0.354</td>
<td>86.2</td>
<td>264</td>
<td>3.1</td>
<td>n.o.</td>
<td>2500</td>
</tr>
<tr>
<td>PP3</td>
<td>1.06</td>
<td>110</td>
<td>879.2</td>
<td>8.0</td>
<td>0.2</td>
<td>250000</td>
</tr>
<tr>
<td>PP4</td>
<td>1.77</td>
<td>95.4</td>
<td>1257.5</td>
<td>13.1</td>
<td>0.28</td>
<td>200000</td>
</tr>
</tbody>
</table>

Figure 3.89 Complex viscosity vs angular frequency measured at 190°C for the propylene/1,9-decadiene copolymers. (Source: Ye et al. Ind. Eng. Chem. Res. 2004, 43, 2860)

The incorporation of a very small amount of 1,9-decadiene significantly changed the complex viscosity curve due to the formation of LCB structure and the increased $M_w$. Compared to the linear polymer PP1, the LCBed polymers PP2-PP4 exhibited much higher viscosity (fig 3.89) in the low-frequency region. The $M_w$ of PP2 (264 kg/mol) increases by 17% compared to that of PP1 (224 kg/mol). Therefore, according to 3.4 power law, PP2 should have 70% higher $\eta_0$.
than PP1, if both were linear polymers. However, experimentally it is observed that $\eta_0$ of PP2 is 180% higher than PP1 (table 3.23), suggesting the presence of long chain branching in PP2. This result indicates that at this polymerization condition LCBed polymer chains can be efficiently generated with a 1,9-decadiene concentration as low as 0.354 mmol/L. Similar result, i.e. increase in zero shear viscosity with LCB was also reported in another paper when LCB was introduced by copolymerization of metallocene iPP with 1.7 octadiene, however, in this report the molecular weight ($M_n$ and $M_w$) were independent of diene concentration (interestingly, an addition of 5 mol% of diene in feed decreased the $M_w$ by 50%). Introduction of 0.5 mol% octadiene to the linear polymer increased $\eta_0$ by 100% without changing the $M_w$.

In section 3.1 it was described that the addition of small contents of long chain branching to the iPP chain via copolymerization with 1,9 decadiene leads to higher nucleation densities and higher overall crystallization rates. The magnitude of increase in the crystallization rate depends on the distribution of LCB introduced by the diene, since the effect is more prominent for the samples of series 1, when the branches are added uniformly to the polymer chain that simultaneously increased $M_w$ (as indicated by the data of overall crystallization rate of the two series, in section 3.1.2). The above observation contradicts the well known influence of branching on the crystallization rates of linear polymers, which is usually opposite, i.e. the rate of crystallization usually decreases with copolymerization or branching. For example, in polyethylene the effect of LCB on the crystallization kinetics has been published by Alamo et al. observed that at a given $T_c$ the LCB containing ethylene-octene copolymer crystallizes at an appreciably slower rate compared to the same copolymer devoid of any LCB.

The crystallization kinetics of three hyperbranched poly(caprolactone)s designated by the authors as HPCL-5, HPCL-10, HPCL-20, where the digits represent the number of carbon atoms in the linear chain between each branch point, were studied in a relatively recent work. The molecular architecture of these polymers corresponds to a hyper-branched type, and the measured molecular weights were basically constant in the series ($M_w$ ranging from 13,000 +/- 3000). Properties such as overall crystallization rates (non isothermal) and zero shear viscosity ($90^\circ C$) were discussed in reference to linear poly(caprolactone) (LPCL) of similar chemical structure and molecular weight to those of HPCL’s (molecular characteristics are given in table 3.24). These data are relevant for a direct comparison with our data on LCB iPPs, therefore, they are presented in some detail.
Table 3.24 Molecular weights of the linear and hyperbranched polycapro lactones

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPCL</td>
<td>10700</td>
<td>14980</td>
</tr>
<tr>
<td>HPCL-20</td>
<td>15700</td>
<td>23550</td>
</tr>
<tr>
<td>HPCL-10</td>
<td>12600</td>
<td>20160</td>
</tr>
<tr>
<td>HPCL-5</td>
<td>11800</td>
<td>21240</td>
</tr>
</tbody>
</table>

Non isothermal crystallization studies revealed that relative to the linear sample, nucleation and growth were retarded for all branched samples except for the HPCL-20, the sample with fewer branches (figure 3.90). The slower crystallization rate of linear polycapro lactone (LPCL) compared to that of the branched polycapro lactone (HPCL-20) was an unexpected behavior because the linear sample consisted of only one long chain with no chain heterogeneity. In order to explain the unusual behavior and understand the reason for the faster crystallization rate of HPCL-20 than LPCL, the authors compared steady shear melt viscosity of the samples. The argument is that molecular motion of the samples in melt state affects the first step of overall crystallization. Figure 3.91 shows the results of steady shear viscosity for HPCLs and LPCL measured at 90 °C.

Figure 3.90 Crystallization half times measured at different cooling rates for the linear and hyperbranched caprolactones. (Choi, et al. Macromolecules, 2004, 37, 3745)
The higher chain mobility of HPCL-20 (as determined from rheology data, figure 3.91) was cited as the cause for the observed increase in the rate of crystallization compared to the LPCL. Following this reasoning, it is surprising to note that though the mobility of the other two hyperbranched polycaprolactones (HPCL-5 and HPCL-10) was higher than LPCL, but their rate of crystallization was lower compared to LPCL (as observed in figure 3.90). Choi et al attributed the above discrepancy to the presence of more frequent chain heterogeneity in the case of the HPCLs with the shorter linear segments and greater number of branches that ultimately hinder the polymer chains from packing regularly for the effective crystallization.

From Turnbull Fisher equation (refer section 3.1), it is known that the rate of crystallization is governed by two factors, free energy required to form the stable nucleus and molecular mobility. At low undercooling surface nucleation limits the crystallization whereas at high undercooling molecular mobility becomes the controlling factor. The opposing temperature dependencies of the two exponential terms results in a maximum in the plot of crystallization rate against temperature. For polycaprolactones, Li et al.\textsuperscript{300} showed a calculated spherulitic growth rate curve vs. temperature giving a maximum at about 12°C, subsequently, Fransson et al.\textsuperscript{301} observed that their nonisothermal results points to peak values ranging from -13°C to 17°C. However, the peak crystallization temperatures for the non isothermal crystallization carried by Choi et al. on the linear and hyperbranched polycaprolactones lies well above the observed maxima in literature (all of them are above 25°C). The Tg (glass transition temperature) of
polycaprolactone is -64°C\(^{301}\), hence the difference Tg-Tc is at least 90°C (25°C +64°C =89°C) for all the samples in Choi’s paper. Therefore it can be concluded that the crystallization in their work was controlled by the nucleation term in Turnbull-Fisher equation and not by molecular mobility, since any temperature above 25°C is far removed from the Tg to impose considerable restriction on molecular movement of polycaprolactone.

The series of LCBiPP studied in this work serve as materials to test if the explanation offered by Choi et al. applies to interpret the enhanced crystallization rates observed in LCB iPPs in reference to the linear behavior. To this end, the melt viscosities were obtained at 210°C as a function of shear rate. The experimental data (the complex viscosity against shear rate) for both series are given in figures 3.92 (series 1) and 3.93 (series 2). These data were extrapolated to zero shear viscosity for a comparison with previous studies. In the first series the molecular weight increases with diene addition, therefore, the presence of LCB (caused by diene addition) can be detected by noting whether the zero shear viscosity of these samples follows the usual 3.4 power law dependence on molecular weight or whether the addition of diene increases the zero shear viscosity beyond expectations from the power law relationship.

![Graph](image)

**Figure 3.92** Complex viscosity vs angular frequency for samples of series 1 measured at 210°C. (■) linear, (▲) 200ppm and (♦) 375ppm.
Figure 3.93 Complex viscosity vs angular frequency for samples of series 2 measured at 210°C. (-) linear, (*) 50ppm (×) 100ppm and (+) 200ppm.

The above figures indicate that the zero shear viscosity increases with the increase in Mw for both the series (as expected according to previous publications). However, in samples of series 1 the Mw increases with LCB; therefore, the effect of LCB on zero shear viscosity could not be isolated from that of Mw. The rheological study of samples of series 2 might provide better insights on the exclusive effect of diene addition (LCB) on chain mobility (in reference to the value of $\eta_0$), since in series 2 there the Mw remains constant with diene addition. The rheological experiment was carried out starting from a shear rate of 0.1 rad/s. Since all the samples (except linear sample of series 1) exhibited non Newtonian behaviour, any extrapolation to zero shear rates would have been erroneous. To avoid this error the values of viscosity at angular frequency of 0.1rad/s (very close to zero shear rates) for samples of series 1 and 2 are taken as representative of the $\eta_0$ value for comparative purposes. These values are listed in table 3.25. A newtonian behavior was observed for the linear sample at low frequencies, facilitating the extrapolation to 0.1 rad/s.
Table 3.25 Zero Shear Viscosity measured at 210°C, and taken as the viscosity value at 0.1 rad/s. Data listed correspond to series 1 and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw (g/mol)×10⁻³</th>
<th>η₀ (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPP150K1.31</td>
<td>150</td>
<td>340</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>203</td>
<td>1500</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>276</td>
<td>2100</td>
</tr>
<tr>
<td><strong>Series 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPP291K1</td>
<td>291</td>
<td>8000</td>
</tr>
<tr>
<td>HLIPP275K1</td>
<td>275</td>
<td>6700</td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>283</td>
<td>7500</td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>247</td>
<td>4800</td>
</tr>
</tbody>
</table>

The η₀ increases with increase in diene content for series 1, whereas there is no dependency of the diene addition on η₀ for series 2. The extrapolated zero shear viscosity of metallocene catalyzed iPP homopolymer (from ref 24) of Mw 180kg/mol at 200°C was found to be 892 Pas. Furthermore, the PP homopolymer studied by Zhu et. al.²⁹⁴ (Mw = 224kg/mol) was observed to have a zero shear viscosity of 900Pas, extrapolated at 190°C. The Mw of the above PP homopolymers are similar to that of IPP150K1.31 (present study), and, both the homopolymers exhibit zero shear viscosity of same order of magnitude compared to IPP150K1.31 (η₀ is 340 Pas at 210°C).

From the rheological study Choi et al. suggested that the higher chain mobility of the hyperbranched polycaprolactone compared to the linear one was responsible for the observed increase in rate of crystallization of the hyperbranched polycaprolactone. However, the rheological study of the samples used for present work (LCBiPP’s) revealed that the mobility of the chain segments in both the series was mainly dependent on molecular weight and especially for series 1 the addition of LCB (coupled with increase in Mw) to the linear polymer raised the zero shear viscosity considerably. Therefore, the explanation given by Choi et. al. in order to justify the observed increase in crystallization rate of the branched polycaprolactone compared to the linear one may apply to the specific case of hyperbranched polycaprolactones, but is not
general and fails for the present study of LCBiPP. In the present study the observed increase of crystallization rate of the H-linked iPP must be due to some other factor, as it cannot be justified from the rheological data by considering the difference in molecular mobility.

The dependency of zero shear viscosity on Mw for the two series of samples was tested in figure 3.94 (the slope and the regression coefficient of the two lines corresponding to series 1 and 2 in figure 3.94 is given in the table as inset). In series 1 the zero shear viscosity of the sample with 200ppm diene is ~350% times higher than the linear (table 3.25); however, if one takes the 3.4 power law dependence with Mw, the difference in viscosity should have only been 80%. Interestingly, the plot of log(\(\eta_0\)) against log Mw has a slope of ~3 for both series. This value is close to the predicted molar mass dependence of 3.4. However, with only three points and a poor linear fit (regression coefficient is 0.88), it cannot be concluded that the zero shear viscosity of the samples of series 1 follows the 3.4 power law dependence with Mw.

![Figure 3.94 Plot of zero shear viscosity (\(\eta_0\)) against Mw for iPPs of series 1 (in blue, \(\Delta\)) and 2 (in red, \(\square\), \(\eta_0\) obtained at 210°C. Error bars are added considering that Mw calculated from GPC data has a ±10% of error involved.](image)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Series 1</th>
<th>Series 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope ((\alpha))</td>
<td>2.98</td>
<td>3.16</td>
</tr>
<tr>
<td>Regression coefficient (R²)</td>
<td>0.88</td>
<td>0.99</td>
</tr>
</tbody>
</table>
For the samples of series 2 the slope of log($\eta_0$) against log Mw line is 3.1. Moreover, unlike series 1, a regression coefficient value of 0.99 for series 2 suggest that the points fit well to the straight line equation. Therefore, it can be concluded that the zero shear viscosity of LCB iPP samples of series 2 follows the usual observed power law dependence on molecular weight for linear samples and hardly any effect of LCB is evidenced. This can further be evidenced by actual calculation, i.e. following 3.4 power law dependence with Mw the difference in viscosity between IPP291K1 and HLIPP275K1 should have been 21% , which is close to the observed difference of 19.5% in zero shear viscosity (8000 compared to 6700) of the two samples. The preferential distribution of H-links to the lower molecular weight chains did not influence the Mw and prevented the Mw to increase in parallel with addition of diene as opposed to samples of series 1. Consequently, the zero shear viscosity of the samples of series 2 is hardly affected by addition of diene.

Apparently it seems that the comparison of zero shear viscosity of the linear and H-linked samples of series 1 evidences the formation of LCB in H-linked samples. However, in series 1 the observed viscosity data are too few (only 3 points) and too much scattered from the theoretical expectation in order to conclude any specific behavior. Whereas, the dependency of $\eta_0$ with Mw adheres to the well known power law for the samples of series 2 despite the presence of long chain branching, this contradicts some of the previous works in polyolefins where the LCB invariably raised the zero shear viscosity at a fixed Mw.289

3.2 Spin lattice relaxation studies from solid state $^{13}$C-NMR

3.2.1 Background and literature review

The details of the method and the relevant equations used to obtain spin lattice relaxation are given in the experimental section. However, it is worth mentioning again here the fact that spin lattice relaxation governs the return of z magnetization to their equilibrium value, and in this process the spin system gives its excess energy to its surrounding “lattice”. Spin lattice relaxation time is a sensitive probe of molecular motion within a molecule, and it can tell us whether a given chemical environment is in a rigid or flexible portion of the molecule.

Few reports have been published regarding the effect of molecular weight on the $T_1$ of polymers. For un-entangled polyethylene samples of very low molecular weight, Mw =
2150g/mol, it was observed that $T_{1C}$ decreases with increase in molecular weight at a fixed temperature, in a temperature range between 130-260°C and larmor frequency\(^{302}\) (data were recorded at both 25 and 75 MHz). In a subsequent paper, the same authors observed that for entangled polyethylene melts\(^{303}\) the $T_{1C}$ is hardly affected with change in mol wt at a fixed temperature and frequency. As a result it can be speculated that the $T_{1C}$ varies with molecular weight up to a certain value of Mw and does not change with a further increase. The precise Mw where this transition occurs depends on the temperature and larmor frequency. A previous study\(^{304}\) reported 5300 g/mol (at 100MHz and 49°C) as the Mw for polyethylene where $T_{1C}$ is no longer a function of Mw.

$^{13}$C NMR gives relaxation times of all the different types of carbons present in the samples. Comparing the relaxation times of linear to that of branched carbons may help us to correlate the difference in chain conformation by the presence of linkages. Since the branch points lies in the amorphous part of the polypropylene molecule consequently the objective of the NMR measurements was the determination of the $T_1$ (spin lattice relaxation) for the carbons of the amorphous phase present in the isotactic polypropylene and then compare the relaxation times of the H-linked and linear samples in order to conclude the effect of H-links on the relaxation time.

### 3.2.2 Analysis of spin lattice relaxation time ($T_{1C}$) of H-linked isotactic polypropylene

The measurement of $^{13}$C spin- lattice relaxation time can be carried out with different pulsing programs. The Torchia sequence has been used to measure long $T_{1C}$ of the crystalline region of isotactic polypropylene\(^{304}\). Saturation and inversion recovery are used to probe $T_1$ of the non-crystalline phase\(^{305, 306}\). Mostly a proton enhanced $^{13}$C induction via cross polarization (cp) process is desired because of its increased signal amplitude which leads to stronger coupling between nuclei, and improves the detection of relatively weak nuclei, such as carbon-13. The relaxation times for the present study were measured using a saturation recovery cp-MAS(magic angle spinning) method. The details of this method can be obtained in reference 307). Magic angle spinning (MAS) can reduce dipolar interaction. The dipolar interaction widens the linewidth of spectra and fine structures cannot be identified. By physically spinning the sample at the magic angle, 54.74°, the interaction can be reduced.

An example of the room temperature NMR spectra of sample HLIPP203K1.18 is given in figure 3.95. A collection of spectras are shown in the figure for HLIPP203K1.18 with decreasing
delay time from top to bottom. From the figure it is observed that with increase in delay time the intensity of the peaks increases suggesting a change in the net magnetization.

**Figure 3.95** Room temperature CP MAS 13C NMR spectra obtained following the sequence of Alamo et al.\textsuperscript{307} for HLPP203K1.18. The delay times (τ, in sec) are indicated for each spectrum.

From the spectra the intensities were picked and a plot of this magnetization against time fitted according to Bloch equation, \( M_z = M_o (1 - e^{-\frac{t}{T_1}}) \) (also given in experimental section, equation 2.4,) leads to the relaxation time, \( T_1 \). In order to fit the magnetization vs delay time data
in the equation we need to have a value for equilibrium magnetization ($M_0$), but it intrinsically possesses a problem. The equilibrium magnetization is a magnitude that is reached asymptotically, and, in the usual range of times used for these measurements, that value may not have been attained. As a result Mathcad (software) 2000 was used to carry out non-linear fittings. This program requires the experimental data of intensities versus time, as well as the algebraic function that is to be fitted and an initial guess for the adjustable parameters. The initial values entered for the fitting parameters ($T_1$ and $M_0$) were those obtained by a linear representation of the data in Microsoft Excel.

The non-crystalline CH$_2$ resonance appears at ~45ppm, it is broad and of low intensity compared to the crystalline CH$_2$ resonance at 44ppm. Owing to the low fractional content of the amorphous region in the samples analyzed, the intensity corresponds to the amorphous CH$_2$ is low and broad. The amorphous CH$_2$ intensity was obtained by hand deconvolution of this peak from the total amorphous and more intense crystalline CH2 intensity, as shown in Fig 3.96.

The resonance of crystalline and amorphous CH carbons does not appear at different ppm. There is a unique resonance for both CH environments at ~27 ppm. Hence, for this carbon the intensities were fitted with a two component expression of the Bloch equation to obtain the respective $T_{1C}$ of amorphous and more ordered interface or crystalline CH carbon. This expression is given by Eq 3.42:

$$M_z = \alpha M_0 \left(1-e^{-t/T_1}\right) + (1-\alpha)M_0' \left(1-e^{-t/T_1'}\right)$$  \hspace{1cm} (3.42)

Where $\alpha$ is the crystallinity, $T_1$ and $T_1'$ are the spin lattice relaxation times of the crystalline/interface and amorphous regions of CH carbon respectively.

**Figure 3.96** Peak deconvolution of the non-crystalline part of CH$_2$ resonance (at $\tau = 0.80$s) for HLIPP203K1.18.
From the experimental results it was clear that magnetization of CH and CH$_2$ group follows the expected saturation recovery curve, but transient NOE are evident for saturation recovery of CH$_3$ carbon since, $T_{1C} \leq T_{1H}$, due to rapid rotation of methyl group. This leads to multi exponential spin lattice relaxation for methyl carbon, as observed previously$^{308}$. Thus, the experimental results for the CH$_3$ carbon was modelled according to Solomon equation in order to compute the $T_1$ values. This equation describes the spin lattice relaxation procedure for a heteronuclear two spin system$^{309}$, leading to the following equation for carbon magnetization,

$$M_z(t)/2M_0 = 1 + \eta/(1-T_{1C}/T_{1H})\exp(-t/T_{1C}) - [1 + \eta/(1-T_{1C}/T_{1H})]\exp(-t/T_{1H})$$

(3.43)

$\eta$ is the NOE factor, $\eta = \gamma_H T_{1C}/\gamma_C T_{1CH}$.

In the fitting of experimental data according to equation (3.43) $T_1$, $\eta$ and $M_0(eq)$ are taken as adjustable parameters.

The fitting of the experimental results according to the above equations using MATHCAD were performed in order to compute the spin lattice relaxation times. The equations used for different carbons were

CH$_2$ carbon- 1 component Bloch equation (2.4)

CH carbon- 2 component Bloch equation (3.43)

CH$_3$ carbon- Solomon equation (3.44)

**Experimental data and fits with equations 2.4, 3.43 and 3.44:**

**Series 1**

![Graph(a)](image1)

![Graph(b)](image2)

**Figure 3.97** Results of fitting the experimental data with respective exponential functions for IPP150K1.31 (a) Amorphous CH$_2$ carbon (~44 ppm) (b) CH carbon, 2 component fit (~26 ppm) (c) CH$_3$ carbon (~22 ppm)
Figure 3.97- continued

Figure 3.97 Results of fitting the experimental data with respective exponential functions for IPP150K1.31 (a) Amorphous \( \text{CH}_2 \) carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH\(_3\) carbon (~22 ppm)

Figure 3.98 Results of fitting the experimental data with respective exponential functions for HLIPP203K1.18 (a) Amorphous \( \text{CH}_2 \) carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH\(_3\) carbon (~22 ppm)
Figure 3.98 – continued

![Figure 3.98](image)

**Figure 3.98** Results of fitting the experimental data with respective exponential functions for HLIPP203K1.18 (a) Amorphous CH$_2$ carbon (~44 ppm) (b) CH$_2$ carbon, 2 component fit (~26 ppm) (c) CH$_3$ carbon (~22 ppm)

![Figure 3.99](image)

**Figure 3.99** Results of fitting the experimental data with respective exponential functions for HLIPP276K1.15 (a) Amorphous CH$_2$ carbon (~44 ppm) (b) CH carbon, 2 component fit (~26 ppm) (c) CH$_3$ carbon (~22 ppm)
Figure 3.99 – continued…

![Curve Fitting](image)

**Figure 3.99** Results of fitting the experimental data with respective exponential functions for HLIP276K1.15 (a) Amorphous CH$_2$ carbon (~44 ppm) (b) CH carbon, 2 component fit (~26 ppm) (c) CH$_3$ carbon (~22 ppm)

The results for the samples of series 1 are listed in table 3.26.

**Table 3.26** $T_{1C}$ values for the carbons indicated of samples of series 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene (ppm)</th>
<th>$T_1$ (CH$_2$-am*) (s)</th>
<th>$T_1$ (CH-am) (s)</th>
<th>$T_1$ (CH-in**) (s)</th>
<th>$T_1$ (CH$_3$) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>0.51</td>
<td>0.20</td>
<td>11.00</td>
<td>0.77</td>
</tr>
<tr>
<td>HLIPP203K1.15</td>
<td>200</td>
<td>0.89</td>
<td>0.75</td>
<td>82.52</td>
<td>0.77</td>
</tr>
<tr>
<td>HLIP276K1</td>
<td>375</td>
<td>2.42</td>
<td>1.12</td>
<td>496.00</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*=amorphous, **=interphase

The $T_{1C}$ values of the CH$_2$ and CH carbons in the amorphous region for samples of series 1 increase with increase in the level of diene or branching, as seen from table 3.26. The addition of diene (branches) makes the amorphous regions stiffer and more rigid and decreases the
relaxation rate. Kitamaru\textsuperscript{305} and Alamo\textsuperscript{307} previously calculated the value of $T_{1C}$ for amorphous CH$_2$ as 0.18 and 1.27 seconds respectively. The value of amorphous CH$_2$ $T_{1C}$ for the linear and 200ppm samples, listed in table 3.26, lies within the same range (< 1 second). However, compared to these values, the $T_{1C}$ of amorphous CH$_2$ for the sample with 375 ppm diene is five times higher. Since the methyl carbon relaxes much faster, the relaxation is not influenced by diene level. As seen in the Table, the $T_1$ for methyl carbon are comparable for all the samples.

Crystalline and amorphous CH$_3$ also appeared at the same ppm resonance. Compared to the CH$_2$ and CH relaxations, the dynamics of the CH$_3$ carbons in both amorphous and crystalline regions are relatively fast as observed by the full recovery of the CH$_3$ magnetization during the $T_{1C}$ experiment. Hence, the relaxation of LCB iPPs is not influenced by diene level. As seen in Table 3.26, the $T_{1C}$ for methyl carbons are comparable for all the samples.

The cp MAs saturation recovery experiment was also carried out in three of the samples from series 2. These are the linear, LCB iPP with 100ppm diene and LCB iPP with 200ppm diene. $T_1$ values were computed from similar fits and the trend with increase in diene content is analyzed. The following figures illustrate the fits with the pertinent equations for one and two components of the relaxation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{Results of fitting the experimental data with respective exponential functions for IPP291K1 (a) Amorphous CH$_2$ carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH$_3$ carbon (~22ppm)}
\end{figure}
Figure 3.100 – continued

Figure 3.100 Results of fitting the experimental data with respective exponential functions for IPP291K1 (a) Amorphous CH\(_2\) carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH\(_3\) carbon (~22ppm)

Figure 3.101 Results of fitting the experimental data with respective exponential functions for HLIPP283K1 (a) Amorphous CH\(_2\) carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH\(_3\) carbon (~22ppm)
Figure 3.101 – continued

Figure 3.101 Results of fitting the experimental data with respective exponential functions for HLIPP283K1 (a) Amorphous CH$_2$ carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH$_3$ carbon (~22 ppm)

Figure 3.102 Results of fitting the experimental data with respective exponential functions for HLIPP247K1 (a) Amorphous CH$_2$ carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH$_3$ carbon (~22 ppm)
(c) Figure 3.102 Results of fitting the experimental data with respective exponential functions for HLIPP247K1 (a) Amorphous CH$_2$ carbon (~44ppm) (b) CH carbon, 2 component fit (~26ppm) (c) CH$_3$ carbon (~22 ppm)

The results obtained for the samples of series 2 are tabulated in Table 3.27.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene (ppm)</th>
<th>$T_1$ (CH$_2$-am)</th>
<th>$T_1$ (CH-am)</th>
<th>$T_1$ (CH-in)</th>
<th>$T_1$ (CH$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP291K1.31</td>
<td>0</td>
<td>1.02</td>
<td>0.13</td>
<td>4.25</td>
<td>0.79</td>
</tr>
<tr>
<td>HLIPP283K1.31</td>
<td>100</td>
<td>1.14</td>
<td>0.41</td>
<td>6.56</td>
<td>0.80</td>
</tr>
<tr>
<td>HLIPP247K1.31</td>
<td>200</td>
<td>2.56</td>
<td>0.27</td>
<td>7.27</td>
<td>0.77</td>
</tr>
</tbody>
</table>

The $T_{1C}$ values of the CH$_2$ carbons in the amorphous region for the samples of series 2 follows the same trend observed in series 1, i.e. $T_1$ increases with increase in the level of diene or branching, as seen from table 3.27. This increase seems to be proportional to the difference in
Mw, as the $T_{1C}$ for amorphous $\text{CH}_2$ increases from 0.5sec to 1 sec from linear sample of series 1 to series 2 with increase in Mw from 150kg/mol to 291kg/mol.

However the values of $T_{1C}$ for the amorphous carbons of CH are very similar and lie within the experimental error. The spin lattice relaxation time for the interface region is very short in all the three samples and they also are very comparable and probably lie within the experimental error. We may need to increase the delay time to obtain more meaningful $T_{1C}$ values for the carbons in crystalline/interface region. As seen in the Table, the $T_1$ for methyl carbon are comparable for all the samples and the values are similar to those observed for series 1.

Thus it can be concluded that in both the series, with increase in diene content the $T_1$ values of the amorphous region increases with increase in H-linkages indicating the presence of linkages in the amorphous region which stiffens the chain and delays the relaxation compared to the linear samples.

To compare with some of the values of spin lattice relaxation times obtained in the literature, a table is provided below in table 3.28,

**Table 3.28** Data for $T_{1C}$ obtained from literature.

<table>
<thead>
<tr>
<th>Source</th>
<th>Temp (°C)</th>
<th>Frq Used ($^{13}$C)</th>
<th>CH$_2$-a s</th>
<th>CH$_2$-c s</th>
<th>CH-a s</th>
<th>CH-c s</th>
<th>CH$_3$-a s</th>
<th>CH$_3$-c* s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kitamaru</td>
<td>40</td>
<td>50Mhz</td>
<td>62</td>
<td>37</td>
<td>0.27</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kitamaru</td>
<td>64</td>
<td>50Mhz</td>
<td>0.18</td>
<td>64</td>
<td>0.32</td>
<td>42</td>
<td>0.4</td>
<td>1.3</td>
</tr>
<tr>
<td>Randall</td>
<td>40</td>
<td>15Mhz</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>Alamo</td>
<td>27</td>
<td>75Mhz</td>
<td>1.27</td>
<td>1.82</td>
<td></td>
<td></td>
<td></td>
<td>0.47</td>
</tr>
</tbody>
</table>

* crystalline

The fact that spin lattice relaxation time indeed depends on the rigidity of the phase in the sample where it is measured is very clear from the above table, as for each carbon the $T_1$ of crystalline region is significantly higher than that of amorphous one. $T_1$ values listed in table 3.28
also indicates that there are discrepancies among the various the \( T_{\text{1C}} \) values obtained for isotactic polypropylene, especially for amorphous CH and CH\(_2\) carbon. We have already mentioned that in both the series the samples with highest diene displays unusually higher \( T_{\text{1C}} \) value for amorphous CH\(_2\) than the rest. However, when the \( T_{\text{1C}} \) data of amorphous CH obtained in the two series of samples used in the present study is compared with the literature, it is observed that the two linear samples of each series displays somewhat lower value compared to the range observed in the literature. However, the \( T_{\text{1C}} \) of amorphous CH obtained for diene containing samples lies within the range indicated by previous authors. The table also indicates that the \( T_1 \) obtained for methyl carbon was most probably the one corresponding to the crystal phase, as the values obtained in the present study matches exactly with the one obtained by Randall for crystalline component of methyl carbon.

### 3.3 Morphology

#### 3.3.1 Morphology of isotactic polypropylene (Background)

The macromolecular geometry and the way molecules are arranged in a solid are important factors in determining the properties of polymers. From polymers that crumble to the touch to those used in bullet proof vests, the molecular structure, conformation and orientation of the polymers can have a major effect on the macroscopic properties of the material. The general concept of self-assembly enters into the organization of molecules on the micro and macroscopic scale as they aggregate into more ordered structures. Crystallization is an example of the self-assembly process. Polymer morphology is the overall form of polymer structure, including crystallinity, branching, molecular weight and cross-linking.

The chemical structure of Isotactic polypropylene (iPP) is one of the most complex commercially developed polymeric materials, because it has a number of crystal modifications\(^{311}\) such as monoclinic (\( \alpha \)), hexagonal (\( \beta \)), and orthorhombic (\( \gamma \)). The appearance of these three structures is critically dependent upon the crystallization conditions. Actually, commercial iPP grades have crystallized mostly in \( \alpha \) modification. The \( \beta \) form crystallizes only in the presence of nucleating agents\(^{312}\). Polymerization with heterogenous Ziegler-Natta catalyst systems the \( \gamma \) form was obtained only under special conditions, i.e., by crystallization from the melt at elevated pressures (5000atm),\(^{263}\) or by crystallization at atmospheric pressure of low
molecular weight samples\textsuperscript{313}. Gamma form can also be obtained in iPP copolymers containing small amounts (5-20\%) of other olefins\textsuperscript{314,315}.

The crystalline architecture of isotactic polypropylene (iPP) is multifaceted and is manifested on different levels of the structural hierarchy. The morphology of the polypropylene crystals can be classified in three distinctly different levels\textsuperscript{316}. First of all at crystal level, isotactic polypropylene exhibits three major polymorphic forms, $\alpha$, $\beta$ and $\gamma$ (mentioned above). In all these structures the chain conformation is identical and corresponds to the familiar threefold ($3_1$) helix, but differ in unit cell symmetry, inter chain packing and structural disorder. On the intermediate level there are the lamellar structures, which, in the case of iPP can be of differing type both as regards the nature of the lamellae and their mutual arrangement., it has been observed that the $\alpha$-phase crystallizes both from solution\textsuperscript{317} and the melt\textsuperscript{318,319} as a three dimensional array of nearly orthogonal 'cross-hatched' lamellar arrangement. Solution studies have shown the basic structural unit to be a lath-like chain-folded lamellar crystal, these crystals form relatively open networks in solution grown aggregates, but tightly interwoven structures in the melt. $\alpha$iPP exhibits a lamellar branching that is unique in polymer crystallography, and also unique to this specific crystal form. This branching manifests itself under all crystallization conditions and this branching leads to both radial and nearly tangential orientation of lamellae. The cross hatching in alpha form is obtained by nearly orthogonal $\alpha$ branching developing via homoepitaxial growth from parent lamellae. The similar dimensions of the ‘a’ and ‘c’ axis in monoclinic unit cell is responsible for the observation of this cross-hatching in alpha phase of isotactic polypropylene (figure 3.103).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{crosshatch.png}
\caption{Cross hatching in alpha phase (Adapted from, Lotz. et. al, Polymer, 1996, 37, 4969)}
\end{figure}
The branched lamellae grow tangentially from the dominant lamellae at an angle of close to 80°. At this angle there are favorable interactions between the methyl side group of helices that have the same hand. A recent study of the unit cell dimensions of the monoclinic phase formed at high temperatures also indicates that epitaxial crystallization is crystallographically feasible at these temperatures, they observed that the differences in dimension between the a and c axis at low and high crystallization temperatures are small, varying only from 2.3% to 3.5%. The measurement of the thickness of the radial and the tangential lamellae for a highly structurally regular iPP fraction as a function of crystallization temperature revealed that the thin daughter lamellae shows a small variation in thickness with increasing crystallization temperature (75–100Å) while the variation of the dominant lamellae is much greater (100–350Å) in the temperature range of 136-167°C. It was also shown by AFM that the character of the cross hatching displayed at relatively low temperature is quite different than that shown at high crystallization temperatures. At low Tc’s the thickness of both radial and tangential lamellae are comparable whereas at higher Tc’s the cross hatching is composed of thicker, well defined radial lamellae and very thin tangential lamellae.

Studies have shown that isotactic PP’s prepared using metallocene catalyst tend to form a mixture of alpha and gamma phases. The crystal structure of the most common crystal phase of iPP--the α phase was established by Natta and Corradini. The γ phase of iPP had remained rather elusive for many years. It is not usually observed as a different phase, but (co)crystallizes with and within the α phase spherulites. It was first mentioned by Addink and Beintema in 1961, they observed an additional reflection in X-ray powder patterns of low Mw iPP. The real breakthrough in our understanding of the γ phase structure dates from a paper published by Meille and Bruckner in 1989. Meille and Bruckner proposed a structure which departs from common doctrine of polymer crystallography, in that the chain axes in the structure are not parallel (figure 3.104). Instead, the structure is made up of a succession of bilayers tilted 80° to each other.
An alpha phase lamellae can give rise to branching lamellae, which are either in alpha or gamma phase. The branching of gamma phase from the parent alpha has been demonstrated by Lotz.\textsuperscript{264} and it was noticed that lamellar planes of the $\gamma$ phase make an angle of 40° relative to the $\alpha$ phase lamellae (figure 3.105). The structure is unique, in that, although it is composed of sheets of parallel molecules, the molecular orientation in adjacent sheets can be non-parallel.

Morphology of gamma form was also studied in another report\textsuperscript{263}, the study has confirmed the coexistence and concurrent growth of $\alpha$ and $\gamma$ lamellae at the same temperature and pressure. The lamellar thickness of gamma and alpha phase were compared using SAXS
and it was noted that there was a continuous decrease of lamellar thickness with $\gamma$ content. Essentially the specimen containing only $\gamma$ crystals has a lamellar thickness close to half of that of $\alpha$ crystal generated at atmospheric pressure and the same supercooling. Making allowances for the inclination of the gamma phase it was found that the stem lengths of both the phases were close to one another, which suggested that fold structures of the phases were similar. Alamo et al.\textsuperscript{325} studied the morphology of propylene copolymers using AFM. In the paper it was demonstrated that as the fraction of $\gamma$ crystallites increases from 40 to $\geq 70\%$ radially oriented lamellae and intervening cross hatching associated with $\alpha$-iPP, are substituted for heavily tilted $\gamma$ branching. Due to the equivalence in orientation of $\gamma$-i PP branching from parent or daughter $\alpha$-i PP, $\gamma$ rich morphologies appear as a dense array of short lamellae transverse to the macroscopic growth. Additionally, they studied the lamellar thicknesses (long periods) and developed representative histograms of the distribution of long periods for the series of propylene copolymers. From the analysis it was observed that with increasing concentration of defects, paralleling the increase in $\gamma$ content, the distribution becomes narrower and the mean value shifts to considerably lower values. It was suggested that the crystallite thickness decreases with increasing defect content within the series.

A recent study on alpha form lamellae\textsuperscript{326} has demonstrated that the frequency of tangential branching from radial $\alpha$-form lamellae increases with decreasing crystallization temperature. At any given temperature, flat-on and edge-on lamellae grow at the same rate.

A third level of morphology is the spherulitic morphology, lamella grow from a common origin usually in spheric arrangements. Lamellas are the building blocks of spherulites (figure 3.106).

![Figure 3.106 Constituents of crystalline morphology of polypropylene.](image)
Spherulites consist of large number of lamellar crystallites, radiating in all directions from one point, with well defined boundaries. When the spherulites are observed under crossed polaroids in a polarizing microscope, large birefringent regions are seen. The birefringence, of an elongated object is called positive when the refractive index of light polarized parallel to the long axis of the object, \( n_p \), is larger than that of light polarized perpendicular to the long axis, \( n_q \)
\[
\Delta n = n_p - n_q.
\]

Similarly, the birefringence of a spherulite is called positive when the refractive index for light polarized parallel to the radius of the spherulite, \( n_r \), is larger than for tangentially polarized light, \( n_t \)
\[
\Delta n = n_r - n_t \text{ (spherulite)}, \text{ when } n_t > n_r \text{ the spherulite will have negative birefringence.}
\]

Isotactic polypropylene produces lamellae differing in arrangement i.e. radial and tangential lamellae. The optical character (positive or negative birefringence, figure 3.107) depends on two factors, i.e. firstly on the relative proportion of these two populations of lamellae (on frequency of branching) and secondly on the orientation of radial lamella relative to the path of light. The radial lamellae has molecules oriented in the tangential direction and since light propagates along the molecular direction, the spherulites made of preferentially radial lamellae yield negative birefringence (as \( n_r > n_t \)), whereas tangential lamellae have molecules oriented in the radial direction, as a result, spherulites preferentially made up of tangential lamellae yield positive birefringence. The coexistence of regions where radial lamellae are dominant with domains where tangential lamella prevails gives rise to the so called “mixed” spherulites.

The study of spherulites by optical and electron microscopy is a useful starting point from which the broader problems of crystalline morphology and crystallization mechanisms of high polymers can be approached. Padden and Keith classified the spherulites of the iPP in four distinct types according to their morphologies\(^{327}\). Type I and II spherulites belong to the \( \alpha \) form and types III and IV, to the \( \beta \) form. Some later studies\(^{328, 329}\) have shown that Types I and II crystallize with the monoclinic, \( \alpha \), crystal structure whilst Types III to IV crystallize with the hexagonal, \( \beta \), structure. It has been found that the respective rates of nucleation and growth vary for the two crystal phases, hence, they also vary for the corresponding spherulites, quite considerably. Thus, Types III and IV nucleate at a much lower rate than Types I and II, but once nucleated they have 20-70% faster growth rate than types I and II\(^{330}\). These two opposing trends have the consequence that Types III and IV appear with noticeable frequency only below certain
crystallization temperatures $^{331}$ . In another report $^{332}$ it was observed that crystallization of iPP below 132°C produces both $\alpha$ and $\beta$ spherulites, and above that temperature only $\alpha$ spherulites form. Spherulites of the $\alpha$ form have a more complex structure and higher density of crosshatching lamellae than $\beta$ spherulites, which are of open structure and lower density of crosshatching lamellae.

![Diagram showing optical sign of the spherulite](http://example.com/diagram.png)

**Figure 3.107** Optical sign of the spherulite (determined by inserting a lambda plate)

Norton and Keller investigated the morphology of the iPP spherulites $^{85}$ crystallized in the temperature range 100-150°C, by using a polarizing microscope and a transmission electron microscope. They found that each spherulite type is characterized by the arrangement of its constituent lamellae, i.e. the type I spherulite contains the predominant branching lamellae, so the value of birefringence is positive, while the type II spherulite is composed of the predominant radiating lamellae, so the value of birefringence is negative. On the other hand, Bassett and Olley found that the maximum temperature at which cross-hatching was present in spherulites was 155°C $^{333}$ . Observing the spherulites under microscope exhibits large birefringent areas and the differences in the spherulitic nature is governed by chemical structure, molecular weight and crystallization conditions. Later on Alamo et. al. $^{334}$ carried out morphological studies on a well
characterized isotactic poly(propylene) which clearly revealed extensive cross-hatching not only for the samples crystallized at the lowest temperatures, but also in those crystallized at $T_c > 160^\circ$C.

SEM has been used to characterize the spherulitic morphology and differentiate $\alpha$ and $\beta$ type spherulites of isotactic polypropylene$^{335}$. In that paper two kinds of spherulites were differentiated by their contrast, with some dark and the others bright. Using different analytical methods (DSC, X-ray and densitometry) it was proved, quantitatively, that the dark spherulites crystallized in the monoclinic $\alpha$-form, while the bright ones consisted of the hexagonal $\beta$-type. The difference in the observed contrasts is interpreted in terms of the lamellar structure of the individual phases, the $\beta$ lamellae being irregularly twisted, while the $\alpha$ phase is presumably interlocked in a cross-hatched array of radial and tangential lamellae. Therefore, when the specimens are oriented perpendicular to the direction of the electron beam, the $\beta$-surfaces scatter the secondary electrons more efficiently than the $\alpha$-sections, and thus more secondary electrons reach the detector in the former case. Consequently, it appears that the structure of bulk samples of polypropylene can be readily investigated by a simple SEM examination, at a much higher resolution than when using the polarizing microscope.

In bulk crystallized iPP, $\alpha$ and $\gamma$ phases are usually intermixed within any one spherulite and are therefore difficult to distinguish, the $\beta$ phase produces well individualized negatively birefringent spherulites admixed with, and therefore clearly recognizable from the weakly birefringent or positive $\alpha$ phase spherulites. Mezhgani and Philips studied the spherulitic morphology of gamma phase in detail$^{336}$, they demonstrated that $\gamma$ polypropylene forms three different types of spherulites, on the basis of sign of birefringence, as a function of crystallization temperature. Positively birefringent spherulites are observed at both high and low supercoolings, with negatively birefringent species occurring at intermediate supercoolings. The transition zones between the negatively birefringent and positively birefringent species are characterized by the concurrent growth of spherulites with no clearly discernible sign of birefringence, which have been labeled 'mixed birefringence' spherulites. Melting studies of the latter species grown in the vicinity of the higher temperature transition showed that they changed into clearly positively birefringent spherulites during the melting process. The results of optical microscope, SEM, and AFM studies showed that positive spherulites grown in the upper temperature range were composed of a unique feather-like structure. This feature, which has never been reported for any
polymer, is unique to the $\gamma$ form. In addition, the SEM, the AFM, and the birefringence results indicated that the feather-like structure was solely developed by self-epitaxial growth of the $\gamma$ lamellae.

In a recent publication\textsuperscript{337} the morphology of long chain branched isotactic polypropylene (crystallized from melt) was documented. The authors however, did not specified the method of LCB addition to the linear polymer. The results indicated that the morphology of LCBPP depends strongly upon the crystallization condition. Crystallization of the LCBPP during the fast cooling process, or at lower crystallization temperature, leads to the formation of mainly edge-on lamellar structure. Crystallizing LCBPP at moderate temperature range results in the formation of both edge-on and flat-on LCBPP crystals, which coexist side by side even in the same spherulite. The content of flat-on crystals increases with increasing crystallization temperature. The LCBPP crystals grow, however, slower than their linear counterparts and the crystal growth rates of both PPs are temperature dependent.

The spherulitic morphology has been studied for long chain branched cis 1,4 polybutadiene\textsuperscript{92}, in the report they have presented spherulitic features of melt crystallized cis 1,4 polybutadiene with different levels of long-chain branching at different crystallization temperatures. Of particular interest is the observation of what the authors called 'dwarf" (small) spherulites in the highly branched cis 1,4 polybutadiene sample. These dwarf spherulites stopped growing at a size of several microns and induced new dwarf spherulites along its periphery. The formation of dwarf spherulites appears related to the suppressed growth rate and the stronger tendency of induced nucleation in the long chain branched samples. The decreased growth is attributed to a decreased chain mobility with increasing branching.

3.3.2 Morphology of H-linked isotactic polypropylene

It has been documented that both branching and molecular weight influences the morphology of semi crystalline polymers. The effect of branching and molecular weight on the spherulitic and lamellar morphology was studied in the present work. Changes in the polymorphic ratio influence the spherulitic and lamellar morphology;\textsuperscript{338} therefore, in the present work the morphology of the isotactic polypropylene samples was studied after crystallizing them at different $T_c$, in order to investigate the effect of polymorphic contents on the morphology. The effect of long chain branching on the supermolecular structure was analyzed by crystallizing the
linear as well as branched samples under identical conditions and observing them under optical microscope.

Recently, AFM has been recognized as a useful tool for the characterization of lamellar growth of semicrystalline polymers. A comprehensive report of AFM study on crystallization of isotactic polypropylene from the melt has been published recently\textsuperscript{326}. The lamellar growth behavior of \(\alpha\) and \(\beta\)-form i-PP spherulites were observed in situ and in real time using AFM at elevated temperatures. While some of the work is already available in the literature, it is reported here in greater detail. More importantly, the missing detail for the crystallization of the \(\alpha\)-form is presented, as well as new information concerning the \(\beta\) form.

### 3.3.2.1 Spherulitic morphology

The samples were allowed to crystallize from quiescent melts in a range of crystallization temperatures (Tc), detailed in experimental part. In figure 3.108 an attempt was made to obtain the optical microscope images of the three samples (series 1, crystallized at 140\(^\circ\)C) at the point when the spherulitic structure starts appearing initially. It can be observed from the micrographs that the number of spherulites per unit area (spherulitic density) increases with increase in diene content; moreover, the samples with diene, figure 3.108 (b and c), form a granular heavily nucleated structure or clusters of supermolecular structure without any specific pattern.

![Initial supermolecular structure of samples from series 1](image)

(a) 0 ppm 140\(^\circ\)C (35 min)  (b) 200 ppm 140\(^\circ\)C (16 min)  (c) 375 ppm 140\(^\circ\)C (11 min)

**Figure 3.108** Initial supermolecular structure of samples from series 1. The crystallization temperature and times are indicated.
A similar study conducted in the samples of series 2 led to linear and diene containing samples with spherulitic structure, as shown in Figure 3.109. The nucleation density also increases with increase in diene content in this series.

![Figure 3.109 Initial supermolecular structure of samples from series 2. The crystallization temperature is indicated and times varied from 25 min to 30 min.](image)

The samples of series 1 were then allowed to crystallize isothermally and the optical micrograph images of the three samples were taken after crystallizing them sufficiently, till the heat of fusion value does not change as a function of time, at each Tc.

**IPP150K1.31**

![Figure 3.110 Final supermolecular structure of IPP150K1.31 (linear sample, series 1)](image)
The linear sample of series 1 exhibited well developed spherulitic structure as shown in figure 3.110 for Tc>125°C, highly quenched materials are formed below that Tc. This indicates the well organized lamellar structures within the spherulites at Tc’s greater than 125°C. With the increase in Tc the diameter of the spherulites increases drastically (from ~60µm at 120°C to ~600µm at 150°C).
Figure 3.111 Final supramolecular structure of HLIPP203K1.18 (200 ppm, series 1)
The well developed supermolecular structure cannot be observed for the diene containing samples in series 2 (figure 3.111 and 3.112). It can be speculated that a combination of two factors, extremely high nucleation densities and higher molecular weight compared to the linear one, prevents the formation of well-developed spherulitic structure in the H-linked iPPs. At 150°C for the sample with 200 ppm diene (figure 3.111f) some spherulitic structure can be observed since the crystallization time is longer at this high temperature, which in turn provides sufficient time for the lamellas to be organized thereby forming spherulitic structure.

**HLIPP276K1.15**

(a) $T_c = 110^\circ$C  
(b) $T_c = 120^\circ$C  
(c) $T_c = 130^\circ$C  
(d) $T_c = 135^\circ$C

**Figure 3.112** Final supermolecular structure of HLIPP276K1.15 (375 ppm, series 1)
The supermolecular structure of the sample with highest diene containing sample (HLIPP276K1.15, figure 3.112) is very different from that of HLIPP203K1.18. A cluster of nuclei (perhaps some gels) are observed for HLIPP276K1.15 at almost all the Tc’s, even at 150°C spherulite formation is not observed.

From the variation with temperature of the optical micrographs it can be concluded that the uniform introduction of diene to linear iPP changes the supermolecular structure drastically, whereas when the diene is introduced selectively to the shorter chains of the polymer, as seen in figure 3.109 of series 2, the spherulite formation is preserved since the nucleation density does not increases to the extent of disrupting the order in supermolecular structure.

The birefringence of the spherulites of the linear sample of series 1 was also studied. Samples crystallized at Tcs 120-150°C have mixed-type birefringence. This may be explained from the ratio of polymorphic content present at the respective Tc. The gamma content is between 30-50% in this Tc range, then the formation of almost equivalent amounts of radial and tangential lamellae makes the birefringence a mixed type as shown in figure 3.113.
A comparison of the spherulitic morphology of the samples of series 2 isothermally crystallized is given in figure 3.114. Unlike the very different spherulitic morphologies, i.e. final supermolecular structure, observed in the linear and diene containing samples of series 1, the final supermolecular structure at 135°C for the linear and diene containing samples in series 2 is not very different. The main reason for this discrepancy in the two series can be attributed to the increase in the nucleation density of the diene containing samples in series 1. The nucleation density difference between the linear and diene containing samples in series 2 is much narrower, thereby allowing the formation of well developed spherulitic structure with mixed birefringence (figure 3.114) in all the diene containing samples of series 2.

Figure 3.113 Mixed type birefringence of linear, series 1 IPP150K1.31 as a function of increasing Tc.
3.3.2.2 Lamellar morphology

The lamellar morphology was studied using Atomic force microscopy. Polymer films of 30-50 microns were sandwiched between round microscopic slides in order to prepare samples for morphological studies by AFM. The microscopic slides were then placed in evacuated tubes and subsequently melted in a silicone oil bath at 200°C for 15-20 minutes and then quickly transferred to a second silicone oil bath maintained at the required crystallization temperature. The crystallization temperature and times used were similar to the samples crystallized for WAXS studies. For AFM scanning, one of the cover slip was removed very carefully to ensure no damage is done to the surface of the samples for subsequent examinations.
It has been demonstrated from previous studies that the changes in the polymorphic ratio influence the lamellar morphologies\(^{325}\). We are then interested in the morphology of the samples crystallized at different isothermal crystallization temperatures to investigate the effect of polymorphic contents on the morphology. The changes in the lamellar thicknesses at different crystallization temperatures was studied in order to evaluate the effect of long branching on the structure of the crystals that develop under isothermal and non-isothermal conditions, structural changes are also expected between \(\alpha\) and \(\gamma\) crystals.

The lamellar features, cross hatching or other lamellar branching and crystallite thickness was be quantified using AFM from the phase images.

Figure 3.115 displays phase images for the linear sample of series 1 (iPP150K1.31) as a function of crystallization temperature (from 100-150°C). It is quite apparent from these images that the lamellar thickness increases with increasing Tc. The phase image at Tc = 140°C (figure 3.115e) is too blocky and relevant information regarding the lamellar long period could not be deciphered from this image.

**IPP150K1.31 (AFM Phase images)**

![Phase images](image)

(a) Tc = 100°C, 1×1\(\mu\)m (26\%\(\gamma\))                                (b) Tc = 120°C, 2×2\(\mu\)m (42\%\(\gamma\))

**Figure 3.115** Lamellar morphology of IPP150K1.31
The morphology at the lamellar scale is expected to exhibit the cross hatching typical of the alpha phase along with tangential gamma branching. However, given that the level of gamma content is in the range of 30 to 60%, it is very difficult to isolate stack of lamellas pertaining to pure gamma form from the cross-hatched combination.

Cross-section profiles from the AFM images, generated by the Jeol AFM process software as seen in the examples below, were used to estimate thickness of lamellar long periods. These measurements were obtained from edge-on crystals, and measured from valley to valley on the profiles of the phase images. A representative example is given in Figure 3.116. At least
80 crystallites were measured in each specimen. The data were plotted in the form of histograms using half the standard deviation as the bin width. Histograms for the linear iPP of series 1 are shown in figure 3.117.

Figure 3.116 Representative examples of section profiles for measurements of lamellar thickness. Phase image of iPP150K1.31, crystallized at 135°C

Figure 3.117 Representative histograms of lamellae long spacings showing distributions obtained from AFM measurements for iPP150K1.31, crystallized at different Tc’s.
Figure 3.117 – continued
Figure 3.117 – continued

Figure 3.117 Representative histograms of lamellae long spacings showing distributions obtained from AFM measurements for iPP150K1.31, crystallized at different Tc’s.

In general the thickness distributions for iPP150K1.31 appear broad and asymmetric at all Tcs. The distribution appears unimodal at 100°C, 135°C and 150°C, whereas at 125°C and 120°C the distribution is broader and is bimodal, this may be an indication of the two types of crystallites (alpha and gamma). It is also observed that, except for 135°C, with increase in temperature the mean value of lamellar thickness shifts to considerably higher values, and especially at 150°C lamellae of thickness around 600Å are observed.

There are large uncertainties the thickness measurements by AFM. This is due to the intrinsic errors associated with the diameter of the tip and, for these samples with the presence of two polymorphic forms. It is also difficult to identify the exact lamellae orientation given that both $\alpha$ and $\gamma$ phases coexist in almost equal proportions for most of the samples analyzed. Lamellar thickness analysis for the linear sample of series 1 (IPP150K1.31) is presented below (figure 3.118). This analysis may need some corrections as the lamelli pertaining to gamma form were not isolated and the thickness and periodicity of $\gamma$ lamellae that grow at 40° from the radial axis is, however, different by 1.55 ($1/\sin40^\circ$). Hence, a careful selection of lamellae with clear orientations will be further needed. This could not be done in the AFM images obtained.
The lamellar morphologies of HLIPP203K1.18 was studied as a function of crystallization temperature in figure 3.119. The morphology of the diene containing sample seemed to be different from the linear one. Blocky structures are detected, and the lamellas are edge on (figure 3.119c), cross hatching was seen only at Tc = 125°C. Though at all the crystallization temperatures the content of gamma was above 50% but still hardly any tangential lamellae could be isolated, moreover the overall lamellar organization seems to be disrupted compared to the more organized lamellar structure of the linear sample.
Lamellar morphologies of the sample with highest diene content (375 ppm) in series 1 were examined using AFM at different isothermal crystallization temperatures. The representative figures at 120 and 130°C are shown in figure 3.120. Similar to the other diene containing sample, the lamellar structure for HLIPP276K1.15 seemed to be disorganized and tangential lamellae could not be isolated, also no cross hatching was observed.
From the morphology presented in figures 3.115 (linear), 3.119 (200 ppm) and 3.120 (375 ppm) it can be concluded that similarly to the supermolecular morphology, the addition of diene to the linear sample disturbs the organized lamellar morphology and produces somewhat blocky and irregular structures disrupting the general pattern observed for the linear sample.

The molecular weight increases in parallel to the addition of diene in the samples of series 1. As a result, the disorder observed in the lamellar morphology of the diene containing samples in series 1 may result from either the diene addition or molecular weight or it may be a synergistic effect of the two combined factors. In the samples of the series 2 the molecular weight remains virtually unaffected and there is hardly any observed trend of molecular weight with increasing amount of diene addition. The lamellar morphology of the series 2 samples is shown below as a probe of the effect of diene addition on the lamellar organization, independent of the molecular weight effect.

The lamellar morphologies of the four samples of series 2 are compared in figure 3.121 under identical isothermal crystallization ($T_c = 135°C$), from the AFM phase images.
It is observed that the linear as well as the diene containing samples exhibit a spherulitic morphology and the difference in the supermolecular morphology was minimal. However, comparing the lamellar morphology of the same samples it is observed that linear sample exhibits a well defined lamellar structure where tangential lamellas pertaining to gamma form can also been seen (figure 3.121a), whereas the diene containing samples do not exhibit ordered lamellar structures. For LCB iPP with 200ppm of diene, blocky lamellae are (figure 3.121d). Blocky structures have also been observed with the 200ppm diene containing sample of series 1 (figure 3.119a, d).
In view of the relatively featureless AFM images of isothermally crystallized specimens, the morphology of the LCB iPPs was also compared with that of linear samples under a different crystallization mode, this is by cooling from the melt at at 1°C/min. Figure 3.122 shows the morphologies of series 2 crystallized under this condition.

![Images of AFM images showing lamellar morphology](a) IPP291KI (0 ppm), 1×1µm (b) HLiPP275K1 (50 ppm), 1×1µm (c) HLiPP283K1 (100 ppm), 1×1µm (d) HLiPP247K1 (200 ppm), 1×1µm

**Figure 3.122** Lamellar morphology of samples of series 2 cooled at 1°C/min.

The lamellar morphology of the linear sample (figure 3.122a, crystallized at 1°C/min) is very well organized. The cross hatching pertaining to the alpha phase is distinctly observed. In line with the lamellar morphologies observed for the diene containing samples crystallized
isothermally (figure 3.121 b, c, d), the morphologies of the same samples on crystallizing non isothermally are not as well defined. The sample with lowest diene content (figure 3.122 b) exhibits edge on lamellas whereas the other two (figure 3.122 c and d) have disorganized and blocky lamellar structures.

From the study of lamellar morphologies of the two series it can be inferred that the linear sample in both the series (though having a wide difference in molar mass) produces well defined and organized lamellar morphologies exhibiting cross hatching pertaining to alpha phase and in some instances the tangential lamellae pertaining to gamma phase could also be isolated. However, the diene containing samples in both the series, independent of molecular weight effect, produces much disorganized, blocky lamellar structure. It appears that the introduction of long branching into the linear iPP distorts the lamellar organization and produces poorly formed lamellae in the diene containing samples.

3.4 Dynamic mechanical analysis

3.4.1 Background

Molecular mobility in amorphous or crystalline structures can be stimulated by systematic variation of the applied dynamic mechanical excitation and by temperature variation. Variable parameters are temperature, frequency, and the amplitude for dynamic and static loads. The study of the dynamic parameters over a wide range of temperatures and frequencies provides an insight into the structure of polymers, including correlating impact stability and damping, measuring glass transition and secondary transition temperatures.

DMA provides valuable data for characterizing the properties of materials, particularly polymers. DMA measures the amplitude and phase of the displacement of a sample in response to an applied oscillating force. The stiffness of the sample is calculated from this data and converted to a modulus to enable property evaluation. Tan δ, the loss tangent or damping factor, is also calculated. A temperature scan at constant frequency can generate a fingerprint of the material’s relaxational processes and its glass transition temperature (Tg). This technique provides valuable data on polymer structure.

The storage modulus E’ (elastic response) and loss modulus E” (viscous response) of polymers are measured as a function of temperature or time as the polymer is deformed under an
oscillatory load (stress) at a controlled (isothermal or programmed) temperature in a specified atmosphere. The dynamic storage modulus, $E'$, is approximately similar to the Young or elastic modulus, or stiffness. As expected, the elastic modulus or stiffness at a particular temperature increases with increase in density (i.e., crystallinity), this can be attributed to the fact that for a given polymer density, the stiffness at higher temperatures is lower, because of enhanced molecular motions and any increase in crystallinity/density reinforces the amorphous matrix and thus reduces molecular mobility, which in turn is reflected in a higher $E'$. The stiffness of polymer, although primarily influenced by density, also increases slightly with molecular weight, most likely because of increased entanglement density.

The dynamic loss modulus or viscous modulus, $E''$, is a measure of the energy absorbed due to a relaxation and thus is useful in clarifying the mechanisms of internal motions and the loss modulus to damping and energy dissipation. The damping or dissipation factor, tan δ, being the ratio of the dynamic loss (or viscous) modulus to the dynamic storage (or elastic) modulus, provides information on the relative contributions of the viscous and elastic components of a viscoelastic material, proportional to the ratio of energy lost to energy stored in one cycle.

Any linear or branched polymer usually display a series of transitions, in addition to melting, which can be detected by dynamic mechanical analysis. In order of decreasing temperature, below the melting temperature, these have been conventionally designated as the $\alpha$, $\beta$ and $\gamma$ transitions or relaxations.

All these peak transitions correspond to different motions in the polyethylene chain. The $\gamma$ transition requires lowest energy and occurs at the lowest temperature (in the range of -150 to -120°C) due to motion in amorphous portion, this has been associated with the Tg of polyethylene. Khanna et al. suggested that the $\gamma$ relaxation involves the motion of a short segment of amorphous polyethylene in addition to the reorientation of loose chain ends within the crystalline and amorphous fractions. The $\beta$ relaxation occurs between -30 and 10°C depending upon the type of polyethylene. The $\beta$ transition has been attributed to the segmental motions in the interphase. The $\alpha$ transition is usually found between 30 and 120°C. It is of common believe that the $\alpha$ transition is representative of the crystalline phase and originates from some type of motion within crystals. The incorporation of structural and chemical factors into the chain such as bromination, chlorination, branching or copolymerization with noncrystallizable counits reduce the level of crystallinity and thus decrease the intensity of
this transition and its peak shifts to lower temperature. Changes in the intensity of this transition with the level of crystallinity have been demonstrated by dynamic mechanical methods for bulk crystallized polyethylene. As a reference the variation of loss modulus for various polyethylenes is shown in figure 3.123.

![Figure 3.123 Dynamic loss modulus $E''$ vs. temperature of various polyethylenes (Source, Khanna, Y.P; Türi, E.A; Taylor, T.J; Vickroy, V.V; Abbott, R.F; Macromolecules, 1985, 18, 6, 1302)](image)

Similarly for polypropylene, the relaxation occurring at the lowest temperature (requiring lowest energy), is attributed to the $\gamma$-relaxation and is assigned to the local mode relaxation in the amorphous phase. The $\gamma$ transition is characteristic of segment movements (rotation of methyl groups) in main or side chain, as this type of rotation requires least energy compared to segmental motions. The iPP $\gamma$ transition is found at $\sim -100^\circ C$. In iPP copolymers, an increase in branching (comonomer content) reduces the intensity of $\gamma$ transition and shifts it to lower temperatures.

The main iPP relaxation found around $0^\circ C$ is attributed to a $\beta$-relaxation. This has generally been attributed to the glass transition ($T_g$) of the polypropylene, since in polyethylene $\gamma$ transition is associated with $T_g$, as opposed to polyethylene, below which the cooperative segmental mobility of the polymer chains are arrested. The $\beta$ relaxation is assigned
to the cooperative segmental mobility of disordered chains\textsuperscript{344, 345}. Usually its intensity increases with the increase in comonomer content\textsuperscript{346}. Additionally, it has been proposed that the $\beta$ transition results from the onset of diffusional motion of branch points\textsuperscript{347}, consequently branching enhance $\beta$ transition.

The third transition that is usually be observed in the range 35-90\degree C is attributed to the $\alpha$-relaxation and has generally been co-related with the crystalline phase. $\alpha$-Relaxation is due to motion of segments of the chain unit which lie within the crystalline portion of the polymer. The temperature and intensity of $\alpha$-relaxation peaks increase with increase in lamellar thickness\textsuperscript{348}.

An example of dynamic mechanical analysis of isotactic polypropylene is shown in figure 3.124. All the three peaks are observed, $\alpha$ peak between 35-70\degree C, $\beta$ peak between 0-30\degree C and $\gamma$ peak around -100\degree C.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{dynamic_mechanical_spectrum.png}
\caption{Dynamic mechanical spectrum of i-PP (1Hz) (Source- Feng, Y; Jin, X; Hay, J.N; \textit{Journal of Applied Polymer Science}, \textbf{1998}, Vol. 68, 395)}
\end{figure}
3.4.2 DMA of H-linked isotactic polypropylene

Copolymerization of isotactic polypropylene with 1,9 decadiene (even at the ppm level) produces long chain branching\(^{37}\), affecting, as shown earlier the rheological properties to a substantial extent. Previous studies\(^{343-345}\) demonstrated that copolymerization or branching also affects the mechanical properties (loss and storage modulus) and changes the intensity and position of the transition peaks. In this section we probe the effect of copolymerization (in ppm levels) and molecular weight on the mechanical properties of isotactic polypropylene, as inferred from DMA data. DMA transitions of samples in the two series are analyzed. The storage and loss modulus in viscoelastic solids measure the stored energy, representing the elastic portion, and the energy dissipated as heat, representing the viscous portion. As the material goes through its glass transition, the modulus reduces, i.e. with increase in temperature the material becomes less stiff.

DMA data was obtained for slowly cooled samples. The crystallinity was estimated from their DSC meltings, as shown in figure 3.125 (series 1) and figure 3.126 (series 2). Crystallinity plays a major role influencing the modulus values and intensity of the transition peaks for semicrystalline polymers.

![Figure 3.125 DSC meltings of the samples (used for DMA) of series 1 at 10°C/min.](image)
The multiple peaks observed in the melting thermograms are due to the presence of different polymorphic forms, the heat of fusion and crystallinity values obtained from the thermograms are listed in table 3.29 for the samples of both the series. There is hardly any difference in the crystallinity obtained from the heat of fusion of the samples as evident from table 3.29.

In the present study the transitions of three samples of the series 1 (linear, 200ppm diene and 375 ppm dine) and three from series 2 (linear, 100ppm diene and 200ppm diene) are analyzed using dynamic mechanical methods. As expected and in accordance with the crystallinity values the difference in storage modulus of the samples in each series [figure 3.127 (series 1) and figure 3.128 (series 2)] is also minimal. For comparison the storage modulus values of each of the samples at room temperature (25°C) are provided in table 3.30.
Table 3.29 Transition temperatures and crystallinity of samples of series 1 and 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene (ppm)</th>
<th>Defects (mol%)</th>
<th>Transition peaks obtained from figure 3.129 and 3.130 (Tan delta vs Temperature)</th>
<th>ΔH (J/g)</th>
<th>Xc (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>1.31</td>
<td>β 2.60</td>
<td>96.80</td>
<td>96.08</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>200</td>
<td>1.18</td>
<td>α 6.62</td>
<td>91.57</td>
<td>100.20</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>375</td>
<td>1.15</td>
<td></td>
<td>79.95</td>
<td>98.40</td>
</tr>
<tr>
<td>Series 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IPP291K1</td>
<td>0</td>
<td>1</td>
<td></td>
<td>87.67</td>
<td>99.01</td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>100</td>
<td>1</td>
<td></td>
<td>91.38</td>
<td>99.46</td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>200</td>
<td>1</td>
<td></td>
<td>90.50</td>
<td>98.32</td>
</tr>
</tbody>
</table>

* Crystallinity (Xc) for each sample is obtained on dividing the ΔH value by 209 J/g.

Figure 3.127 Storage Modulus as a function of temperature for samples of series 1
The loss modulus of the samples are plotted in figure 3.129 (series 1) and figure 3.130 (series 2). Knowledge of the temperature dependence of the modulus (loss and storage) gives most important clue to the engineering application of a polymer. The temperature scan of loss and storage modulus for the three samples of each series is depicted from figure 3.127-130. The temperature dependence is characterized by a shallow decline of the modulus ($E'$ or $E''$) over
most of the scan with a few abrupt drops along the entire range. The shallow decline is due to thermal expansion, the molecules in the solid move further apart as the temperature increases, and this lowers the modulus. Each abrupt drop is generated by a viscoelastic relaxation process due to some specific type of molecular movement. Beginning at a certain temperature the shear storage and loss moduli are observed to drop sharply (especially $E'$). This is due to a change in internal structure of the crystallizing polymers at temperatures close to the melting point.

**Figure 3.129** Loss Modulus as a function of temperature for samples of series 1

**Figure 3.130** Loss Modulus as a function of temperature for samples of series 2
High molecular weight and crystallinity stiffens the polymer and increases the modulus\cite{339,347}. In the present samples the difference in molecular weight or crystallinity are not significant enough to influence the intensity of loss or storage modulus to a large extent. A slight decrease in storage modulus is observed in the diene containing samples in series 1 as compared to the linear one (the difference is \(~500\text{MPa at }25^\circ\text{C}\) as molecular weight increases from 150K to 200K. It is known that crystallinity is the main factor influencing $E'$, and, as calculated from heat of fusion values, there is hardly any difference in the crystallinity of the diene containing samples compared to the linear one. As a result the difference in $E'$ can be regarded as within the experimental error associated with the measurements.

In series 2 we observe an opposite trend, i.e. with increase in diene the storage modulus increases slightly but the magnitude of difference in absolute values is less compared to difference observed for samples in series 1 (at 25°C the difference is \(~250\text{MPa}\). The increase seems to be more logical since the H-links may act as crosslink and increase the stiffness which ultimately influences the absolute value of $E'$. The loss modulus seems to be unaffected by the diene addition especially after 0°C. In support of our results a report can be cited\cite{346}, where it has been demonstrated that addition of LCB by constrained geometry catalyst (CGC) has little effect on loss or storage modulus values in case of ethylene propylene copolymers.

The loss tangent ($\tan \delta$) curves as a function of temperature for the three samples are shown in fig 3.131 (series 1) and 3.132 (series 2), two transitions, $\alpha$ and $\beta$ in the order of decreasing temperature, were observed, the third transition ($\gamma$) occurs at temperature lower than the range of temperature used in our experiment (~100°C.). $\tan \delta$ is particularly important for polymers because it is related to the material's ability to dissipate energy in the form of heat.

Increasing temperature the molecule transits from a tightly compressed state to a more mobile one and the material warms and expands, the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur. Here (-100°C) is where the gamma transition occurs. As the temperature and the free volume continue to increase, the whole side chains and localized groups of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughnes. As heating continues, Tg or glass transition is reached ($\beta$ transition), where the chains in the amorphous regions begin to coordinate large-scale motions. One classical description of this region is that the amorphous regions have begun to melt. Since the Tg only occurs in amorphous material, in a 100%
crystalline material we would not see a \( T_g \). Continued heating brings to \( \alpha \) transition that occurs in crystalline or semicrystalline polymer and is a slippage of the crystallites past each other. Finally, we reach the melt where large-scale chain slippage occurs and the material flows, this is the melting temperature, \( T_m \).

The temperature of \( \alpha \) transition peak observed in both series of samples (table 3.28) agrees well with the temperature range (60-110\(^\circ\)C) as determined in previous studies with metallocene iPP’s\(^{345,349}\). A strong relation exists between \( \alpha \) transition and crystallinity, and the intensity of transition decreases with decrease in crystallinity. The H linkages lie in the amorphous region leaving the crystalline portion almost unaffected, therefore, minimal difference is expected between the nature (peak position and intensity) of \( \alpha \) transitions of the linear and branched samples in both the series. It is quite evident from fig 3.131 and 3.132 that according to our expectation the intensity and position (table 3.29) of \( \alpha \) transitions are almost identical and they overlap each other. In accordance with previous studies for metallocene catalyzed iPP\(^{349,350}\), the \( \beta \) transition (for the polypropylene samples chosen in this work) was found to occur between \(-10\pm10^\circ\)C. The \( \beta \) transition results from the motion of segments in the amorphous region and the H-links produced by diene addition are also present in the amorphous portion, as a result the segmental motion of the amorphous part of H-linked samples might be different from those present in linear samples. Accordingly, it is observed in fig 3.131 that the addition of diene to the linear iPP increased the intensity of \( \beta \) transition in series 1 and shifted it to slightly higher values (listed in table 3.29). This behavior is analogous to the observed behavior of long chain branched ethylene/propylene copolymers compared to iPP as reported earlier\(^{346}\). In case of series 2 the change in the peak position is not significant, though the intensity decreased slightly with addition of diene.
Rheological studies from sheared melt and crystallization studies from quiescent melts evidenced that the addition of diene in ppm levels has a big influence on the resulting rheological properties and crystallization behavior. However, the DMA studies on the same samples indicates minimal variation in the modulus values (loss and storage) and transition positions on addition of diene to linear iPP, basically suggesting that the resulting semicrystalline structure is not much affected by ppm of diene addition. The close proximity of molecular weight and
minimal variation in crystallinity among the samples may be cited as the probable reasons for the observed behavior.

3.4.3 Determination of Crystallinity using InfraRed (IR) Spectroscopy (Samples used for DMA)

The measurement of crystallinity by DSC has errors associated with drawing the baseline to compute the total heat of fusion. A test of DSC values and of the minimal variation among the linear and LCB samples was undertaken by IR crystallinity measurements of the samples prepared for DMA analysis.

Since Natta et al.\textsuperscript{351} first synthesized high molecular weight isotactic poly(propylene) (iPP) in 1955, the IR spectroscopy has been used to elucidate the structure of this crystalline polymer. Measurement of polypropylene isotacticity by IR spectra has been carried out by various authors\textsuperscript{352, 353, 354}. Recently, Lamberti et. al.\textsuperscript{100} reported crystallinities for isotactic polypropylene using IR spectroscopy.

The crystallinity of the two series of samples studied in the present work was measured using the method described (IR) in experimental section. The results are tabulated below for series 1 and 2 in table 3.31. The crystallinity obtained by DSC is also compared with the values from IR.

Table 3.31 Crystallinity of samples of series 1 and 2, measured by IR and DSC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diene (ppm)</th>
<th>Xc % IR</th>
<th>Xc % DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPP150K1.31</td>
<td>0</td>
<td>70</td>
<td>45</td>
</tr>
<tr>
<td>HLIPP203K1.18</td>
<td>200</td>
<td>70</td>
<td>48</td>
</tr>
<tr>
<td>HLIPP276K1.15</td>
<td>375</td>
<td>68</td>
<td>47</td>
</tr>
<tr>
<td>IPP291K1</td>
<td>0</td>
<td>65</td>
<td>47</td>
</tr>
<tr>
<td>HLIPP283K1</td>
<td>100</td>
<td>66</td>
<td>48</td>
</tr>
<tr>
<td>HLIPP247K1</td>
<td>200</td>
<td>66</td>
<td>47</td>
</tr>
</tbody>
</table>
From the table it is clear that the difference in crystallinity between the linear and H-linked samples, measured by IR as well as DSC, in both the series is insignificant. Therefore, it can be concluded that the long chain branching and its distribution does not have any effect on the crystallinity. The discrepancy in absolute values of the crystallinity obtained from IR and DSC can be explained by considering that the crystallinity measured by DSC takes into account only the core crystallinity values, whereas the crystallinity measured by IR incorporates the contribution of the interphase region in addition to the core crystallinity. Therefore, the crystallinity obtained from IR is always higher in magnitude than those obtained from DSC under identical crystallization condition.
CHAPTER 4
CONCLUSIONS

In this work the effect of very small concentrations of diene (0 – 400 ppm) added to the iPP chain on the crystallization, polymorphism and morphological behavior of two series of copolymers of this nature crystallized from their quiescent melts was analyzed. The LCB was added in the linear chain via copolymerization with 1, 9 decadiene. The introduction of ppm level of LCB leads to higher nucleation densities and higher overall crystallization rates. The magnitude of increase in the rate depends on the distribution of LCB introduced by the diene. From the polymorphic analysis a difference in the LCB distribution was evidenced between the two series of samples. In the series with uniform inter-chain LCB content the longer chains are the most branched ones. The branched polymers of this series exhibited higher difference in nucleation density compared to the linear sample. However, in the series where LCB is preferentially placed in the shorter chains, the difference in nucleation density with the linear iPP is significantly lower.

Proportional to the increase in nucleation density, a significant increase in the overall crystallization rate was observed for the diene containing samples, especially when the diene was added uniformly. However, the linear growth rates, which are not affected by primary nucleation, are very similar for the homopolymer and its H-linked copolymers in accordance with the small variation in the total content of defects in these materials. This minimal variation in growth rate confirms that the addition of ppm levels of diene does not change the chain structure as to impact the growth.

The increase in $^{13}$C spin lattice relaxation time of the amorphous region with addition of branches, as evidenced from solid state NMR, indicates that the presence of linkages in the amorphous regions slows short segmental relaxations of the diene containing samples in this region compared to the linear ones. This delay in relaxation of the chains of H-linked samples may be instrumental in retaining some order in the molecules prior to crystallization from their melt and can be speculated as the most probable cause for the wide difference in nucleation rate observed. However, the crystallinity was not affected by the addition of LCB, as indicated from DSC, WAXS and IR analysis.
No significant differences in the crystal geometry between the linear and H-linked iPP were obtained from the analysis of overall crystallization kinetics from quiescent melt using Avrami model. Three dimensional crystal geometry was observed for the linear as well as diene containing samples. However, the application of Avrami model to the crystallization rate data for the same set of samples from sheared melts indicated very different growth geometry from the H-linked samples compared to its linear counterpart. Crystallization from sheared melts suggested that the spherulitic crystal geometry for the linear sample transforms to disklike and finally becomes rodlike with increase in LCB. Moreover, poor fits of the experimental data of isothermal crystallization kinetics from quiescent melt with the theoretical single–stage models improved by application of a two stage model, and provide indirect evidence of the simultaneous development of the α and γ polymorphic forms in the samples studied.

The formation of the gamma polymorph is an inverse function of the average length of continuous isotactic sequences in the iPP chain; hence, the content of gamma crystals is found to be sensitive to the structural changes in the iPP chain due to the presence and distribution of H-linkages LCB. In reference to the linear chain, and due to the irregularities introduced in them by addition of diene, iPPs with up to 400 ppm diene content develop about 15% higher contents of crystals in the gamma phase. The spherulitic morphology was particularly affected when the random addition of small contents of diene to longer chains increased the nucleation density and molecular weight significantly. However, the well organized lamellar morphology of the linear iPP is greatly affected by the addition of diene irrespective of its distribution. H-linked iPP’s exhibited blocky and irregular structures disrupting the general pattern lamellar branching pattern observed for the linear sample.

Dynamic mechanical studies indicated minimal variation in the mechanical properties with the addition of diene to linear iPP, basically indicating that the difference in molecular weight or crystallinity that occurs by addition of ppm levels of diene to the linear sample is not sufficient enough to influence the mechanical properties as studied by DMA.
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BIOGRAPHICAL SKETCH

Anindya Kumar Ghosal was born in Kolkata, State of West Bengal, India. In July 1999, he received his Bachelor of Science degree in Chemistry and subsequently in August 2002, he received his Bachelor of Technology degree in Polymer Science and Technology from University of Calcutta, India. He joined Florida State University to pursue PhD in Chemical Engineering. His research field being crystallization and morphology of long chain branched isotactic polypropylene. From June-August 2007 he worked as an intern at Shell Global solutions, Houston, in their polytrimethylene terephthalate department. He is joining Shell Technology India as a Technology Development Engineer from March 2008.