COMPARATIVE STRUCTURE DEVELOPMENT OF VARIOUS POLYOLEFINS IN INJECTION MOLDING PROCESS

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COMPARATIVE STRUCTURE DEVELOPMENT OF VARIOUS POLYOLEFINS IN INJECTION MOLDING PROCESS

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Dissertation

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ABSTRACT

We have investigated structure development of various polyolefins in the injection molding process, which include high density polyethylene (PE), isotactic polypropylene (PP), isotactic polybutene-1 (PB1) and isotactic poly(4-methyl pentene-1) (P4MP1). Orientation, morphology and crystallization variation along thickness direction of molded part were studied under varying processing parameters: volumetric injection rate or injection pressure, packing pressure, and thermal condition based on mold and inlet melt temperatures.

The effort to account for these variations on structure development was combined with considerations of quiescent crystallization kinetics and rheological properties of raw materials. The order of crystallization rate from fast to slow was found out to be PE > P4MP1 > PP > PB1. The relaxation behavior of each polymer chain was studied to consider the amount of chain relaxation before crystallization from melt state and explain resulting orientation development.

In order to make objective and quantitative comparisons in structure development of different materials or even the same material with different crystallization and rheological behavior, it was necessary to apply equivalent stress since crystalline orientation and morphology are determined by applied stress fields. From the
effort to provide equivalent mechanical stress during molding process, we could find out that the level of orientation during mold filling is highest in P4MP1 under same level of stress applied, then PB1 > PP > PE, which is consistent with the earlier Ph.D. dissertation of C.H. Choi for melt-spinning study. A mathematical model was developed to represent the relationship between the levels as well as the modes of orientation in melt state and in the molded parts after crystallization. The orientation state is represented by a second order tensor, $O_{ij}$. Different crystalline orientation states in crystallized polymers as compared to the melt are represented by a 4$^{th}$-order tensor, $S_{ijkl}$ which varies with the materials.
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CHAPTER I
INTRODUCTION

Injection molding is one of the most important polymer processing operations in terms of development of new product designs and the investigation of microstructure developed in injection molding has been significant issues for long period.

During the molding cycle consisting of filling, packing and cooling stages, the polymer melt experiences a complicated thermo-mechanical history associated with material properties, mold and delivery system geometries, and molding conditions. This complex history determines the final microstructures of injection-molded articles and it is very important to investigate the mechanism of structure development since the final microstructure directly influences the physical, optical and mechanical properties of injection-molded articles. In injection molding semi-crystalline polymers, complex heterogeneous morphologies have been found to occur from high shear and normal stresses, and thermal gradient through the thickness direction. Close to the surface of the molded part, a fine morphology with a reasonably high state of orientation forms and a spherulitic microstructure with reduced orientation is observed at greater depths into the molded part, where the stress history has been relatively mild and the polymer melt is allowed to cool down slowly.

Polyolefins are very important thermoplastics that comprise the largest portion of the world’s commercial polymers and have attracted many researchers. These include
two major thermoplastics of polyethylene (PE) and polypropylene (PP) and two lesser known thermoplastics of polybutene-1 (PB1) and poly(4-methyl pentene-1) (P4MP1) as well as their copolymers. The chemical structures of these polymers are shown in Figure 1.1, where asymmetric carbon atoms are indicated with asterisks.

![Chemical structures of various polyolefins](image)

Polyethylene and these three isotactic polyolefins are commercially available (Syndiotactic polypropylene is also commercially available). They possess the indicated crystalline melting points. As the side group of isotactic polyolefins becomes longer than isotactic polypropylene, they exhibit lower and lower melting points. Polypentene-1 has a
crystalline melting point of 75 °C and polyhexene-1 is practically amorphous at ambient temperature. Introducing methyl group onto the linear side group raises the crystalline melting point. Poly(4-methyl pentene-1) has a melting point of 235 °C, whereas poly(3-methyl butene-1) is 300 °C, which is too high for chemical stability.

There have been many studies of structure development in injection-molded polyolefin parts. These were primarily for polyethylene and polypropylene. There have been a few studies on isotactic polybutene-1 and poly(4-methyl pentene-1). In the present study, a quantitative and comparative study in structure development of these four polyolefin materials in injection molding process was carried out. We seek to investigate the structural differences through the cross-sections of these molded parts among these polyolefins and the reasons for these differences.
CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Crystal Structure

Various crystal modifications have been found to occur in polyolefins, which is known as polymorphism. We are going to investigate possible crystal modifications arising in each polyolefin in this section.

2.1.1 Polyethylene

Polyethylene (PE) generally gives rise to the stable orthorhombic unit cell when it crystallizes from the melt and solution at atmospheric pressure. This crystal modification with parallel methylene chains with all trans chain conformation was first studied by Muller [1] for \( n \)-hydrocarbons in 1928. He determined the crystal structure of a single crystal of the hydrocarbon \( \text{C}_{29}\text{H}_{60} \) by using wide-angle X-ray diffraction (WAXD) technique and found it to be orthorhombic. He also found many other \( n \)-paraffins are orthorhombic. Muller [2] also observed that many \( n \)-paraffins transformed to a hexagonal unit cell at temperatures near their melting points. The orthorhombic \( n \)-paraffin exhibited strong X-ray diffraction peaks in the planes of (110), (200) and (020). Subsequently, Muller and Lonsdale [3] found a second crystalline form in \( \text{C}_{18}\text{H}_{38} \) which they concluded was triclinic and would occur in other even paraffins. As noted by Smith [4], blends of \( n \)-paraffins are generally orthorhombic.
After low density polyethylene (LDPE) was first produced by ICI in the 1930’s, Bunn [5] investigated its crystal structure and found the Muller orthorhombic structure with the unit cell dimensions of \(a = 7.40 \text{ Å}, \ b = 4.93 \text{ Å} \) and \(c = 2.53 \text{ Å}\). Swan [6] and Davis et al. [7] later investigated the crystal structure of the newly developed linear polyethylenes, high density polyethylene (HDPE) in the 1960’s and described the same unit cell with all \textit{trans} chain conformations as found by Muller [1] and Bunn [5]. The crystal density is predicted to be \(0.998 \sim 1.000 \text{ g/cm}^3\).

A monoclinic crystalline phase in linear polyethylene, first described by Teare and Holmes [8] and Turner-Jones [9], is found to form when the polymer is subjected to tension or compression stress beyond the yield point. Subsequently, Flory [10] and Mandelkern [11] also identified the monoclinic modification in a number of annealed polyethylenes. Seto et al. [12] investigated the monoclinic crystalline form in polyethylene from deformation process by transverse compression. The calculated unit cell parameters were \(a = 8.09 \text{ Å}, \ b = 2.53 \text{ Å}, \ c = 4.79 \text{ Å}, \) and \(\beta = 107.9^\circ\), where \(b\)-axis was considered to be the chain axis. More recent investigators [13,14] confirmed results from early studies above by observing that the monoclinic crystalline phase in linear polyethylene forms under several different conditions such as shear induced crystallization, phase transformation, deep undercooling and epitaxial crystallization from dilute solution. This crystalline modification exhibited three strong 2-theta X-ray diffraction peaks at the \(d\)-spacings of \(4.56, 3.84 \) and \(3.55 \text{ Å}\), compared with \(4.13, 3.72 \) and \(2.98 \text{ Å}\) for the three strongest reflections of the orthorhombic form. The identification of the monoclinic modification, however, can be uncertain for
polyethylenes which are not highly crystalline, since it seldom constitutes more than ten percent of the total crystallinity of the polymer [14].

Basset et al. [15] has found that high density polyethylene (HDPE) melt crystallizes into a hexagonal crystalline form at high pressures and temperatures (ca. 5000 kg/cm², 240 °C) with unit cell dimensions of \( a = b = 4.80 \ \text{Å} \) and \( c = 2.45 \ \text{Å} \). This crystalline form was found to transform to the orthorhombic structure at lower pressures and temperatures.

2.1.2 Isotactic Polypropylene

Isotactic polypropylene has been found to be polymorphic and exhibit \( \alpha \), \( \beta \), and \( \gamma \) crystalline forms as well as a mesomorphic (smectic) structure.

Natta and Corradini [16] carried out the first crystallographic study of isotactic polypropylene in 1955 ~ 1960 and determined the most stable monoclinic \( \alpha \)-structure, which is obtained from the melt or solution crystallized samples. The \( \alpha \)-structure was found to involve balanced 3/1 positive and negative helices of trans-gauche\(^+\)-trans and trans-gauche\(^-\)-trans chain conformations arranged in a balanced manner in the monoclinic unit cell of \( a = 6.65 \ \text{Å} \), \( b = 20.96 \ \text{Å} \), \( c = 6.50 \ \text{Å} \), and \( \beta = 99.3^\circ \), where the \( c \)-axis corresponds to the polymer chain or helix axis. The crystalline density is 0.922 g/cm\(^3\) and there were strong X-ray peaks from the planes of (110), (040), (130), (111) and (131) have \( d \)-spacings of 6.26 Å, 5.19 Å, 4.77 Å, 4.19 Å and 4.04 Å, respectively.

Shortly afterwards, Keith et al. [17] and Addink and Beintema [18] identified the hexagonal \( \beta \)-crystalline form, which has a crystalline density of 0.922 g/cm\(^3\) and exhibits
two strong X-ray reflection at d-spacing of 5.53 Å and 4.17 Å. In crystallization of conventional isotactic polypropylene grades, the α modification is essentially formed which may be accompanied by a lower or higher amount of the hexagonal β-crystalline, of which degree of content is feasible to control by using selective β-nucleating agents or various undercooling [19,20]. Various hexagonal unit cells with different numbers of polypropylene chains have been proposed. Keith et al. [17] suggested a basal parameter $a = 12.74$ Å and an axial parameter $c = 6.35$ Å. Addink and Beintema [18] argued for $a = 6.38$ Å and $c = 6.35$ Å. Turner-Jones et al. [21] also suggested four different hexagonal unit cells with the $a$-axis dimension varying from 11.01 Å to 25.43 Å and the $c$-axis dimension always 6.35 Å. The positive and negative helices are arranged in a slightly different manner in the hexagonal β-crystalline form, which also consists of the same 3/1 helices.

The γ-crystalline form was first observed by Addink and Beintema [18] and as with the β-crystalline form, various arguments have been made over the unit cell by Addink and Beintema [18], Turner-Jones et al. [21], Morrow and Newman [22] and Bruckner and Meille [23]. The view of the latter authors is now generally supported. They proposed an orthorhombic unit cell with $a = 8.54$ Å, $b = 9.93$ Å and $c = 42.41$ Å and a crystalline density of 0.939 g/cm$^3$. The γ-modification has been observed in degraded, low molecular mass polypropylene or in samples crystallized under high pressure [18,21,22,24]. It was also found more recently that high molecular weight isotactic polypropylene may tend to crystallize in the γ-modification, when prepared by employing metalloocene catalyst
systems [25]. Subsequently, Phillips et al. [26] argued that the \( \gamma \)-crystalline form is associated with the chemical heterogeneity in the polypropylene chain caused by lower tacticity or by copolymerization. They also demonstrated that the \( \gamma \)-modification is produced at elevated pressures from high molecular weight homopolymers and has the same diffraction patterns as the low molecular mass polymers crystallized at atmospheric pressure, confirming that the \( \gamma \)-modification is not the result of some unexpected degradation reaction at elevated pressures. The \( \gamma \)-crystalline form has been the subject of extensive study since its very unique structure is composed of sheets of parallel chains just positioned next to one another so that non-parallel chains are generated normal to the sheets [23,27].

Mesomorphic (smectic) isotactic polypropylene was first prepared by Natta and his coworkers [28] by quenching molten isotactic polypropylene in ice water. This mesomorphic form gives rise to two diffuse X-ray diffraction peaks at 5.99 Å and 4.19 Å, which are different from both the crystalline peaks and the amorphous halo. The interpretation of this intermediate structure has been disputed. Natta et al. [28] described this form as smectic, and suggested that it is composed of parallel 2 \( \times \) 3/1 helices but that disorder exists in the packing of the chains perpendicular to their axes. Miller [29] proposed that the quenched form is paracrystalline, whereas Wunderlich [30] classified it as a conformationally disordered crystal. On the other hand, Corradini et al. [31] indicated that in quenched isotactic polypropylene a fairly high correlation of distances is present within each chain and between neighboring chains to form small bundles. The local correlations between chains are probably nearer to those characterizing the crystal
structure of the monoclinic form than to those characterizing the structure of the hexagonal form. This mesomorphic form transforms to the monoclinic $\alpha$-structure when annealed at temperatures above 80 °C [32].

2.1.3 Isotactic Polybutene-1

Isotactic polybutene-1, first synthesized by Natta and his co-workers [33,34] in 1954, is also renowned for its crystal polymorphism. Since early work by Natta et al. revealed the existence of two different crystalline forms referred to as Form I and Form II, various crystalline forms of isotactic polybutene-1 have been proposed. Natta et al. found that a stable hexagonal Form I has a three fold helix with $a = 17.7$ Å and $c = 6.5$ Å. There also exists an unstable tetragonal Form II of a four fold helix with $a = 15.0$ Å and $c = 20.9$ Å [33,34].

The density increases from phase transformation from 0.90 g/cm$^3$ in Form II to 0.95 g/cm$^3$ in Form I. Turner-Jones et al. [35] suggested that Form II has a tetragonal unit cell with $11/3$ helices. They concluded that the unit cell was tetragonal with $a = 14.85$ Å and $c = 20.6$ Å. Zannetti et al. [36] found a third polymorph, known as Form III by precipitating the polymer from various solvents.

Holland and Miller [37] reported that Form I actually exists in two variants, named I and I’, depending on the way it is produced. Form I refers usually to a crystal modification that is generated via a solid-state transformation of Form II, whereas Form I’ refers to the same crystal structure obtained by direct crystallization. The difference may not be trivial, since their melting temperatures have been reported to be significantly
different ($T_m$ for Form I $\approx 130$ °C and $T_m$ for Form I’ $\approx 95$ °C). Nakafuku et al. [38] observed another modification, Form II’, which showed the same X-ray diffraction patterns as Form II, by crystallization under high pressure above 2 kbar. They found that upon heating under high pressure above 2 kbar, there exists a solid-solid transformation from Form II’ to Form I.

Isotactic polybutene-1 generally crystallizes from the melt into Form II, which appears to be kinetically favored. Upon cooling, however, it transforms spontaneously into the thermodynamically stable Form I [35]. This transformation takes about one week under normal conditions and is reflected in important changes in the physical-mechanical changes from increases in density, crystallinity, hardness, rigidity, stiffness and tensile strength. This transition also involves a change in the chain conformation. The 11/3 helix of Form II converts into a 3/1 helix of the Form I. Such a structural change requires an elongation of helical axis.

2.1.4 Isotactic Poly(4-methyl pentene-1)

Isotactic poly(4-methyl pentene-1) exhibits complex polymorphic behavior with five different crystalline forms. The various forms differ from the conformation of the polymer chains and from the mode of packing of chains having the same conformation. The different modifications can be obtained by changing the crystallization conditions, nature of solvent, solution concentration, thermal history of the solution, and cooling rate. Crystallization from the melt only generates Form I, whereas crystallization from solution promotes various crystalline forms [33,39].
Form I appears to be the most stable crystalline modification. It has been found in most melt-crystallized samples and in extruded fibers. It is characterized by chains in 7/2 helical conformation packed in a tetragonal unit cell with axes $a = 18.66 \, \text{Å}$ and $c = 13.80 \, \text{Å}$ [33,40,41]. The density values calculated from the unit cell parameters were found to fall between 0.828 and 0.832 g/cm$^3$. A rather higher, amorphous density, 0.838 g/cm$^3$ was reported. The low packing density of helical molecules in the crystalline regions has been attributed to explain this unusual density behavior [42,43].

The other crystalline forms beyond Form I are usually obtained from crystallization in semi-dilute solutions depending on the solvent and the thermal history of the solutions [39,44]. A tetragonal unit cell with axes $a = 19.16 \, \text{Å}$, $c = 7.12 \, \text{Å}$ and chains in 4/1 helical conformation has been proposed for Form II by Takayanagi et al. [45] from X-ray diffraction patterns in single-crystal mats.

De Rosa et al. [46,47] has refined and determined the crystal structure of Form III. In this crystalline form, chains in 4/1 helical conformation are packed in a tetragonal unit cell with axes $a = 19.46 \, \text{Å}$, $c = 7.02 \, \text{Å}$. De Rosa et al. [46,47] proposed low symmetry packing model of Form III and considered this structure as an example of the phenomenon of symmetry breaking, for which a mode of packing with low symmetry may occur even in the case of polymers which crystallize in highly symmetric single crystals. Charlet et al. [44] observed that Form III transforms into Form I after annealing at $\approx 100 \, ^\circ\text{C}$ and under stretching. De Rosa et al. [46,48] also proposed a 3/1 helical conformation of the chains for the hexagonal Form IV with axes $a = 22.17 \, \text{Å}$, $c = 6.5 \, \text{Å}$. 
More recently, De Rosa et al. [49] presented a new crystal structure of Form II by using X-ray powder diffraction data and packing energy calculations. They calculated that the chains in 4/1 helical conformation are packed in a monoclinic unit cell with axes $a = 10.49 \, \text{Å}$, $b = 18.89 \, \text{Å}$, $c = 7.13 \, \text{Å}$ and $\beta = 113.7^\circ$. It was also found that this structure provides an example of low symmetry in polymer crystals since the local 4/1 helical symmetry of the chains is not maintained in the lattice as crystallographic symmetry, and as a consequence, the chains do not pack in a tetragonal lattice, as generally occurs for chains in 4/1 helical conformation, but are packed in a monoclinic lattice having low symmetry.

2.2 Supermolecular Structure

Before 1957 when Till [50], Keller [51] and Fischer [52] succeeded in growing single crystal lamellae by cooling hot, dilute solutions of polyethylene in xylene, the structure of semicrystalline polymers had been understood by the fringed micelle model, in which individual polymer chains traverse regions of both order and disorder, going from a small crystallite, to an amorphous region, into another crystallite, and so on. Electron micrographs of the single crystal structure demonstrated that the polymer chain axes are perpendicular to the large flat faces and parallel to the thin faces, which enabled researchers mentioned above to hypothesize that the molecules must sharply fold on themselves as the parallel alignment of the chains is almost perfect since the thickness of the crystal is only of the order of 100 Å, while the length of the chains used in the original experiments was of the order of 2,000 Å. This concept of chain folding allowed a
wide range of understanding in structural and mechanical properties of polymeric materials. Subsequently after the first description of the polyethylene single crystal, similar single crystals were formed from dilute solutions of isotactic polypropylene [53-55], polybutene-1 [56], and poly(4-methyl pentene-1) [40,57].

The arrangement of molecular chains at higher level of dimensions is called supermolecular structure which describes organizations of the crystalline and amorphous zones and their associated interfacial regions while crystal structure is called and used to describe the relative portion and orientation of the atoms in the molecular chains. Several superstructure morphologies have been found in crystallizing a polymer such as lamellae, rods, sheet-like structures, hedrites or axialites, and spherulites [58]. These superstructure formations depend on molecular weight, crystallization condition, and structural regularity of the individual polymers and observers. Lamellae and spherulites are most likely to be met in the polymer superstructure [59].

2.2.1 Polyethylene

Detailed characteristics from lamellar and spherulitic structures in polyethylene are described in the following subsections.

2.2.1.1 Lamellar Structure

The lamellar structure of polyethylene single crystals grown from dilute solution became well known after Till [50], Keller [51] and Fischer [52] first described the formation of single crystal lamellae of linear polyethylene. These lamellae were 100 Å thick, which is equivalent to the thickness of about 40 methylene groups. Since then,
extensive studies have been carried out on such crystals and they are known to exhibit well defined fold lengths and habits characteristic of the conditions of growth, depending on different kinds of solvents, crystallization temperatures and molecular weights [60,61].

The effects of crystallization temperature, concentration and molecular weight on polyethylene crystal structure of these lamellae have been investigated. They found that the axial ratio of the crystals increased with crystallization temperature and concentration. Crystals grown from high molecular weight polymers tended to have lower axial ratios than those from low molecular weight material under the same condition.

2.2.1.2 Spherulitic Structure

Generally, spherulites are formed in melt crystallization of polyethylene. Negative spherulites have been well known to form in polyethylene melts, where the angular refractive index, $n_\theta$ is greater than the radial refractive index, $n_r$ [62]. It has also been found by studies of Keller et al. [63] that the spherulites consisted of twisting helicoidal crystallites with angular extinction bands. It later became clear that the twisting crystallites must be folded-chain lamellae because only these could lead to negative spherulites. It was subsequently found that at high pressures above 4 kbar, polyethylene would crystallize into an unfolded, extended chain form [64].

Hoffman et al. [65] observed that a transition of growth rate depends on crystallization temperature at a definite supercooling. About a decade later, Voight-Martin and Mandelkern [66] carried out more detailed studies on the crystallite and supermolecular structure of polyethylene. They observed that the supermolecular structures that are formed depend on the crystallization conditions, the molecular weight
and its polydispersity. They found that it is possible to develop different supermolecular structures either from the same crystallization conditions from different molecular weight polymers or from the same molecular weight materials by choosing certain isothermal or non-isothermal crystallization conditions.

2.2.2 Isotactic Polypropylene

In the following subsections, lamellar and spherulitic structures of isotactic polypropylene are investigated.

2.2.2.1 Lamellar Structure

Well-defined lamellar single crystals of isotactic polypropylene were first grown from solutions [53] but also were obtained from melts [67]. The thickness of these lamellae was about 150 Å with the helical chains perpendicular to the lamellae surfaces. Similar crystals were observed by Sauer et al. [54], Morrow et al. [68] and Kojima [69]. All the lamellar crystal structures from solution and melt-crystallized isotactic propylene exhibited intercrossing branched lamellae structures, leading to the hypothesis of epitaxial lamellar branching, which is unique and not found in other crystalline polymers.

Khoury [55], Binsbergen and de Lange [70] and Lotz and Wittmann [71] made an extensive study on this subject. It was found that the lamellar branching is characterized by an angle of 80° (or 100°) between parent (radial) and daughter (tangential) lamellae. Secondary daughter lamellae grow epitaxially on parent lamellae, sharing the same crystallographic b-axis. Therefore, the chain axis or c-axis of the branched tangential lamellae is nearly perpendicular to the chain axis of primary lamellae. It has also been
found that the degree of epitaxial branching formation decreases with isotactivity and is crystallization temperature, $T_c$-dependent. They reported that the epitaxial lamellar branching occurred below 160 °C and increased with reduced isothermal crystallization temperature.

2.2.2.2 Spherulitic Structure

Isotactic polypropylene spherulites were first described by Padden and Keith [19] in 1959. Padden and Keith [19] and Samuels et al. [72] found that isotactic polypropylene exhibits negative or positive spherulites depending on the crystallization conditions and suggested that five different types of melt crystallized spherulites consisting of $\alpha$ and $\beta$ modifications exist, depending on the crystallization temperature. Three of those five spherulites were positive radial $\alpha_I$ formed below 134 °C, negative radial $\alpha_{II}$ formed above 137 °C, and mixed-type spherulites $\alpha_{III}$ in the intermediate range. It was also found that highly positive birefringent $\beta_{III}$ and negative ringed $\beta_{IV}$, which were crystallized below 128 °C and between 128 and 132 °C, respectively, formed sporadically with $\alpha$ modifications. Subsequent investigators [73,74] supported observations of Padden and Keith [19] with different temperature ranges for the formation of the particular types of spherulites, presumably due to the variability in the molecular characteristics of the isotactic propylene used.

Padden et al. [75] and Binsbergen and de Lange [70] found that the spherulites contained complex arrays of inter-crossing lamellae, which is reminiscent of the single crystals found by Sauer et al. [54] and Khoury [55]. It was hypothesized that the lamellae
growing from the spherulite nuclei exhibited epitaxial growth during crystallization which led to the observation of lamellae inter-crossing [70,76].

2.2.3 Isotactic Polybutene-1

Features of the crystalline morphology of isotactic polybutene-1 are described in its lamellar and spherulitic structures in following subsections.

2.2.3.1 Lamellar Structure

Three different crystal forms were observed in isotactic polybutene-1, prepared from dilute solutions by Holland and Miller [37] in 1964. They found that these three crystalline forms are hexagonal, tetragonal and orthorhombic and the basic morphology of all forms is the thin lamellar structure associated with polymer single crystals containing folded chains. They also stated that during the transformation from the square tetragonal form to the hexagonal or the orthorhombic ones, there was no morphological change involved.

Subsequently, Morrow et al. [77] studied morphological changes in annealing of polybutene-1 single crystals prepared from dilute solutions. With increase of thermal treatment, the shape of crystals changed from lath-shaped to hexagonal and square. They observed spiral growths when crystallization was carried out non-isothermally or at high degrees of supercooling.

Sastry and Patel [78] linked morphologies to three different crystalline forms also observed by Holland and Miller [37]. It was observed that orthorhombic crystals consist
of multilayers with square and lath shape while the crystals with tetragonal and hexagonal modification have square or hexagonal habits and present spiral growths.

2.2.3.2 Spherulitic Structure

The crystalline morphology of isotactic polybutene-1 from the melt has also been investigated. Fuchs et al. [79] and Jandt et al. [80] described needle-like structures in very thin polybutene-1 films drawn from the melt. Silvestre et al. [81] investigated the crystalline morphologies of isotactic polybutene-1 prepared from both isothermal and non-isothermal crystallization. They observed well-defined spherulites in tetragonal Form II from samples isothermally crystallized from the melt. They stated that at isothermal crystallization temperature above 100 °C, some crystallites lose part of the spherulitic character and square crystals appear with hedritic morphology. For samples crystallized during the cooling, the morphology was characterized by large and small spherulites nucleated at different times and temperatures. They stated that the existence of two different kinds of spherulites is attributed to the presence of heterogeneous nuclei having different activation energy.

2.2.4 Isotactic Poly(4-methyl pentene-1)

Morphological features from lamellae and spherulites of isotactic poly(4-methyl pentene-1) are investigated in the following subsections.

2.2.4.1 Lamellar Structure

The morphological structure of isotactic poly(4-methyl pentene-1) (P4MP1) single crystals prepared from dilute solution of several solvents has been known to exhibit
square lamellae [40, 82]. Frank et al. [40] indicated that crystals appeared as pyramidal, some form of polygons or spheres, and dendritic structures depending on the cooling rate. Bassett et al. [82] observed slightly dished square lamellae because of distortion of the subcell by ordered arrangements of folds and bowl-shaped habit developed from concentrated solution.

Geil et al. [57] found the lamellar thickness to be 350 Å for the melt-crystallized P4MP1 in the 201 ~ 235 °C range and presumed lamellae single crystals. They also observed that the solution-crystallized P4MP1 over the range of 25 ~ 90 °C exhibited lamellar thickness about 100 Å. While the annealing did not change the mean lamellar thickness of the melt-crystallized samples indicating an upper limit, solution-crystallized lamella, upon annealing, was found to exhibit lamellar thickening and reach a mean lamellar thickness of 350 Å, which is attributed to the low packing density of P4MP1 in the crystalline state, inducing high chain mobility in the crystal at high temperature.

2.2.4.2 Spherulitic Structure

Griffith [42], Campbell [83] and Saunders [84] found spherulites in P4MP1. No birefringence in the spherulitic superstructure of P4MP1 was observed at temperature up to 50 °C. They also stated that the different temperature dependence of the tangential and radial refractive index resulted in a change in the sign of the birefringence from positive below 50 °C and negative above 50 °C, where the densities of the crystalline and amorphous phases become equal to each other. It was proposed that the $a$-axis of the unit
cell increases at a greater rate with temperature than $c$-axis, bringing the refractive index changes.

Extensive studies on the crystal morphology of melt-crystallized P4MP1 have been carried out by Bassett and Patel [85]. They studied the morphology of P4MP1 spherulites, of which average diameter was 20 $\mu$m. They observed that these spherulites develop from initial square lamellae by iteration of branching and divergence of the two daughter lamellae to give a framework within which subsequent subsidiary lamellae developed. They identified the origin of spherulitic growth as the lamellar divergence at spatially distributed arrays of branch points from the growth of lamellae up to the thickness of 600 Å upon annealing.

More recently, Silvestre et al. [86] obtained various populations of lamellae with different thickness in melt crystallized P4MP1 spherulites, depending on crystallization conditions. They hypothesized that there exist time-dependent sequence of crystallization, resulting in three types of lamellae (type I, II and III). Few very thick lamellae (type I) start to grow from the melt with no dependence on crystallization conditions or annealing, while thick lamellae (type II) formed at crystallization temperature and very thin and defective type III lamellae formed during cooling from the crystallization temperature to room temperature strongly depend on the preparation conditions.

2.3 Crystallization Kinetics

The study of crystallization of polymers is generally conducted in isothermal conditions. The study of crystallization in a continuously changing environment, however,
is also of great interest, since industrial processes generally occur in non-isothermal conditions. In this chapter, therefore, both isothermal and non-isothermal crystallization are investigated.

2.3.1 Isothermal Crystallization Kinetics

Measurement of overall crystallization rate from the crystallite nucleation rate and growth rate involve often the macroscopic determination of crystallinity as a function of time. According to the Avrami expression [87], the overall crystallization kinetics is often described as

\[ 1 - X(t) = \exp(-Kt^n) \]  

(2.1)

where \( X(t) \) is the relative crystallinity at time \( t \), defined by the ratio of the present crystallinity to the final crystallinity attained in the given conditions. \( K \) is called the crystallization rate constant, which is temperature dependent and \( n \) is the Avrami index. The theoretical values of \( n \) are known to be integer for particular mechanisms of nucleation and crystal growth as shown in Table 2.1.

The values of the exponent \( n \) found, however, may be fractional, which have variously been attributed to volume changes on crystallization, incomplete crystallization, annealing, or different mechanisms involved during the process. Constants \( K \) and \( n \) contain information on nucleation, linear growth rate, and crystal geometry, which can be obtained from experimental data by construction of a plot of the relative crystallinity versus time in double logarithmic form as

\[ \log[-\ln(1 - X(t))] = \log K + n \log t \]  

(2.2)
which is equivalent to Eq. (2.1). Morphological observations are still important since they should be carried out to understand microscopic mechanism of crystallization since the Avrami expression only indicates a macroscopic overall data as mentioned above.

Table 2.1 Avrami Indices for Particular Mechanisms of Nucleation and Linear Growth

<table>
<thead>
<tr>
<th>Linear Growth</th>
<th>Nucleation</th>
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<tbody>
<tr>
<td></td>
<td>Homogeneous</td>
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<tr>
<td>Three-dimensional</td>
<td>4</td>
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<tr>
<td>Two-dimensional</td>
<td>3</td>
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<tr>
<td>One-dimensional</td>
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</table>

2.3.1.1 Polyethylene

Extensive studies on the overall crystallization rate of linear polyethylene (PE) have been carried out by numerous researchers [88-91].

Mandelkern et al. [90,91] made the most extensive investigations on the dependence of the overall crystallization rate on chain length. They investigated the crystallization kinetics of PE with molecular weights ranging from 2,900 up to $8 \times 10^6$ and found that deviations from the Avrami theory occur at lower degree of transformation as molecular weight increases. The Avrami exponents were found to be independent of temperature and have integral values, depending on molecular weights. An Avrami exponent value of 4 was reported below the molecular weight of 5,800 and it became 3 with increasing molecular weight up to $1.2 \times 10^6$. For molecular weights over $1.2 \times 10^6$, a value of 2 was found.
The dependence of the molecular weight and the crystallization temperature on crystallization rate was also studied by investigating $\tau_{0.01}$, the time required for 1% of the absolute amount of crystallinity to develop. With crystallization temperatures ranging from 115 °C to 132 °C, it was found that as the crystallization temperature is increased, the maximum crystallization rate is achieved with higher molecular weight and crystallization time decreases several orders of magnitude in lower molecular weight range.

2.3.1.2 Isotactic Polypropylene

The overall isothermal crystallization of isotactic polypropylene (PP) has been a subject of interest, especially the dependence of crystallization half time, $\tau_{1/2}$ on crystallization temperature, $T_c$, molecular weight and degree of isotacticity [92-94]. $\tau_{1/2}$ was found to decrease very rapidly with $T_c$, but have little correlation with molecular mass at a given $T_c$, which agrees with the fact that nucleation density and spherulite radial growth rate were found to have no significant dependence on molecular weights [93].

The influence of degree of isotacticity on the overall crystallization rate of PP was investigated by several researchers [92,94-96]. It was reported that $\tau_{1/2}$ increased with higher degree of isotacticity for a given $T_c$. The effect of the catalyst type, however, was found to be much stronger that that of isotacticity fractions, which Martuscelli et al. attributed to different level of impurities and distribution of stereo-sequences of repeat units with same degree of isotacticity according to the choice of the catalyst.
Avrami analysis has been employed for the crystallization kinetics of PP [94,97]. Avrami exponents between 1.8 and 3.2 were reported and found to increase with decreasing supercooling and decrease with isotacticity at constant supercooling.

2.3.1.3 Isotactic Polybutene-1

An Avrami analysis of the kinetics of bulk crystallization of polybutene-1 (PB1) was carried out by Patel et al. [98]. They found that the kinetics followed the Avrami equation for most of the transformation, with a deviation towards the end of crystallization. The value for the Avrami exponent was about 3 at high undercooling, suggesting a homogeneous nucleation, and around 4 at lower undercooling, perhaps indicating a heterogeneous nucleation.

By calorimetry and microscopy studies, Cortazar and Guzman [99] reported $n = 2$, suggesting a two-dimensional growth rate of the crystal and found that such an exponent is independent of both temperature and molecular weight. They found that the overall crystallization rate increases with increasing molecular weight, whereas Monasse and Haudin [100] found a molecular weight independent linear growth rate. More recently, Acierno and Grizzuti [101] investigated the effect of molecular weight on the crystallization behavior under quiescent, isothermal conditions by rheological and optical microscopy techniques. They found that the crystallization rate of isotactic polybutene-1 is essentially not affected by the molecular weight. They argued that the transition from a chain-folded spherulitic to a chain-extended disk-like morphology, determined by the coupling between crystallization temperature and molecular weight, does not seem to
affect the PB1 crystallization rate, which remains the molecular weight independent both below and above the transition temperature.

2.3.1.4 Isotactic Poly(4-methyl pentene-1)

There has been only a small number of studies on the bulk crystallization behavior of isotactic poly(4-methyl pentene-1) (P4MP1) [42,102-104]. The first study of crystallization rate of P4MP1 was carried out by Griffith et al. [42] in 1960. They reported the value of 4 for the Avrami exponent dilatometrically, whereas values of 3 and 2 were found by Yadav et al. [102] and Silvestre and his coworkers [104], respectively. Whereas there have been different Avrami exponents reported, the relative crystallization rate of P4MP1 has been found to be ranked between polyethylene and isotactic polypropylene [42,103,104].

2.3.2 Non-isothermal Crystallization Kinetics

The crystallization of semicrystalline polymers takes place under non-isothermal conditions in most polymer processes such as fiber spinning, extrusion, injection molding and so on. The study of crystallization under non-isothermal conditions is much more complicated than for isothermal conditions since temperature as a function of time, $T(t)$ must be taken into consideration.

Several methods [105-109] have been proposed, most of which are based on the Avrami equation, in order to study kinetic parameters of non-isothermal crystallization process. We summarize the frequently encountered analyses be earlier investigators in the following subsection.
2.3.2.1 Kinetic Models for Non-isothermal Crystallization

In 1971, Ozawa [105] proposed non-isothermal kinetics modeling for the process of nucleation and subsequent growth by modifying the Avrami equation. He accounted for the effect of constant cooling rate, $\chi$ and the degree of conversion at temperature $T$, $X(T)$ was calculated by

$$\log\left\{-\ln\left[1 - X(T)\right]\right\} = \log K'(T) - n \log \chi$$  \hspace{1cm} (2.3)

where $n$ is the Avrami exponent and $K'(T)$ is the cooling crystallization function, which is related to the overall crystallization rate and indicates how fast crystallization occurs.

Subsequently, Nakamura et al. [106,107] proposed a model based on the isokinetic approximation involving the assumption that the kinetics of primary nucleation and of crystal growth rate are similar so that the ratio of growth rate to nucleation rate is constant. They derived the equation

$$X(t) = 1 - \exp\left[-\left(\int_0^t K'(T) d\tau\right)^n\right]$$  \hspace{1cm} (2.4)

where $n$ is the Avrami index determined form isothermal crystallization data and $K'$ is related to the Avrami constant as $K' = K^{1/n}$.

Patel and Spruiell [108] later suggested a differential form for the Nakamura model which has the form

$$\frac{dX(t)}{dt} = nK'(T)[1 - X(t)]\{-\ln[1 - X(t)]\}$$  \hspace{1cm} (2.5)

where the Avrami index, $n$ should necessarily be evaluated by isothermal experiments. They suggested that the Nakamura model might be more satisfactory for application to
non-isothermal crystallization than other existing models available, in spite of the approximations used to develop it.

Dietz [109] also proposed a kinetic equation for non-isothermal crystallization with consideration of secondary crystallization as

\[ \frac{dX}{dt} = nX(T)(1-X) \cdot t^{(n-1)} \cdot \exp(-aX / (1-X)) \]  

(2.6)

where the exponential factor is introduced to correct for secondary crystallization such as lamellar thickening, crystallization of segregated molecules, some kinds of reorganization in already transformed portions, and the parameter \( a \) lies between zero and one.

2.3.2.2 Polyethylene

The first detailed study of non-isothermal crystallization kinetics of polyethylene was carried out by Nakamura and his coworkers [106,107] in early 1970’s. The changes in crystallinity were measured by observing the integrated intensity of (110) plane in X-ray scattering and analyzed by the theoretical Nakamura model they developed. They found a satisfactory agreement of experimental values of crystallinity with the values predicted from the model.

Mandelkern and his coworkers studied the relationship between morphology and non-isothermal crystallization conditions of linear and branched polyethylene [110]. They showed that various polyethylene morphologies could be achieved under controlled non-isothermal conditions, depending on molecular weight, concentration of branch groups and quenching temperature.

Eder et al. [111] analyzed non-isothermal crystallization data of HDPE and compared experimental data with those from the theoretical model of Ozawa [105]. They
found a deviation from the equation, which could be attributed to factors such as secondary crystallization, the dependence of the lamellar thickness on crystallization temperature and the occurrence of different mechanisms of nucleation. In the same year, Kamal et al. [112] also studied non-isothermal crystallization of HDPE, using the Ziabicki equation and reported that the deviation of the model from the experimental data was less than that of the Ozawa model.

More recently, Supaphol and Spruiell [113,114] has investigated the quiescent non-isothermal bulk crystallization kinetics of HDPE with a modified depolarized light microscopy technique, allowing for studies at average cooling rates of 5 to 2,500 °C/min. The bulk crystallization kinetics, a strong function of cooling rates, was investigated by the Avrami equation and they suggested that there exist spherical growth geometry and instantaneous, heterogeneous nucleation at predetermined sites from the Avrami exponent values near 3.

2.3.2.3 Isotactic Polypropylene

In early 1980’s, Monasse and Haudin [115,116] studied the thermal dependence of nucleation and growth rate in PP from the non-isothermal crystallization experimental data analyzed with the Ozawa model. They found that there exists a transition between homogeneous and heterogeneous nucleation around 122 °C. Homogeneous nucleation and three-dimensional growth was found to take place below the transition temperature with the Avrami exponent, $n$ close to 4 while heterogeneous nucleation occurred above the transition temperature with $n$ close to 3, which was in good agreement with findings from the results of Eder et al. [111].
Burfield et al. [117] investigated the influence of isotacticity on crystallization kinetics of \(i\)-PP and showed that the crystallization onset temperature decreases in step with reduced isotacticity. They also found that samples prepared with supported catalysts (\(\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3\)) show significantly lower crystallization onset temperatures than those from conventional catalysts approximately due to differences in the intermolecular or intramolecular distribution of stereochemical defects.

Lim and Lloyd [118,119] also analyzed the non-isothermal kinetics of nucleated and non-nucleated PPs with the diluent. They found that the crystallization peak temperatures of nucleated samples are higher than those of non-nucleated samples whereas the addition of the diluent brings no change in the crystallization mechanisms in two PPs.

More recently, Ziabicki [120] calculated the ratio between athermal and transient thermal nucleation rates, which were controlled by various temperatures and cooling rates. It was shown that very high value of ratio of athermal to thermal nucleation rate appeared only in the vicinity of melting temperature since athermal nucleation was proportional to \((\Delta T)^5\), indicating conversely strong relaxational effects were present in a wide range of temperatures and cooling rates.

2.3.2.4 Isotactic Polybutene-1

Silvestre et al. [81] analyzed experimental crystallization data with the Ozawa [105] and the Ziabicki [121] models. They found the Avrami exponent, \(n\) close to 3 from the Ozawa model in good agreement with the value from isothermal crystallization, whereas the calculation from the Ziabicki model seemed slightly off from the
experimental result. It was found that the zero-order approximation is not good enough to
describe the non-isothermal crystallization mechanism of PB1. They proposed that the
athermal nucleation might not be negligible.

2.3.2.5 Isotactic Poly(4-methyl pentene-1)

There has been no systematic study of non-isothermal crystallization kinetics of
P4MP1, even though a small number of bulk, isothermal crystallization studies have
been published [42,102,104].

2.4 Polymer Chain Orientation

The phenomenon of the structure and orientation development is encountered in the
fabrication of polymeric materials. Since the mechanical, optical, electrical and other
physical performances of these materials are generally determined by the degree of
molecular orientation, it is necessary to know the distribution of the orientation of the
internal structural units such as crystallites or molecular segments, in order to understand
the anisotropic properties of the fabricated polymer products.

2.4.1 Representation of Orientation

According to the nature of stress fields, preferred molecular alignment would be
introduced by means of uniaxial or biaxial orientation. We discuss the development of
theoretical treatments for these two types of orientation in the following sections.
2.4.1.1 Uniaxial Orientation

Following the first effort of Sisson and Clark [122] to apply wide angle X-ray diffraction to quantitatively measure orientation in early 1930’s, Hermans and his coworkers developed the methods for specification of uniaxial molecular orientation in the 1930’s and 40’s, which has been elucidated and extended in subsequent studies by various researchers [123-125].

The approach of Muller [123] was to specify the orientation in terms of the anisotropy of the polarizability tensor in a system with cylindrical fiber symmetry and orientation distribution function and the magnitude of orientation described by a uniaxial orientation factor as

$$f'' = \frac{3\cos^2 \phi - 1}{2}$$

where $\phi$ is the angle between the chain axis and the fiber axis.

A decade later in late 1950’s, Stein [125] introduced orientation factors with specific application to polyethylene, which are defined for the three crystallographic axes. These are today called the Hermans-Stein orientation factors and defined as

$$f_j = \frac{3\cos^2 \phi_j - 1}{2}$$

where $j$ can refer to the angles $\alpha, \beta,$ and $\epsilon$ between the $a, b,$ and $c$ crystal axes and the $z$-axis. The value of $f_j$ varies from -0.5 to 1.0, corresponding totally perfect orientation perpendicular and parallel to the fiber axis with zero for an isotropy condition. For an orthogonal unit cell, then
(2.9)\[ \cos^2 \phi_a + \cos^2 \phi_\beta + \cos^2 \phi_\varepsilon = 1 \]

(2.10)\[ f_a + f_\beta + f_\varepsilon = 0 \]

2.4.1.2 Biaxial Orientation

In 1958, Stein [126] described biaxial orientation in polymeric films in addition to three orientation functions defined in Eq. (10), introducing three additional orientation functions based upon a set of new angles defined equivalently to Euler’s angles for each of the three axes. The effort was made on orthorhombic polyethylene crystals and the additional biaxial orientation functions are described as

\[ f_\delta = 2 \cos^2 \delta - 1, \quad f_\gamma = 2 \cos^2 \gamma - 1, \quad f_\sigma = 2 \cos^2 \sigma - 1 \]  

(2.11)

where \( \delta, \gamma, \) and \( \sigma \) represent latitudinal angles between the projection of the three axes in the \( XY \)-plane and the \( Y \)-axis where the \( YZ \)-plane is the plane of the film.

Wilchinsky [127] sought to obtain three orientation factors with non-orthorhombic crystal systems such as monoclinic and triclinic, and proposed to represent biaxial orientation by using the mean cosine square value, \( \cos^2 \phi_{hkl,i} \) where \( hkl \) refers to a crystallographic plane of interest and \( i \) an orthogonal reference direction, as a representation of multiaxial orientation.

A decade later Stein’s work [126] in 1967, Nomura, Kawai and coworkers [128] defined a new biaxial orientation factor, using spherical harmonics, associated Legendre polynomials and Euler’s angles. A newly defined biaxial orientation factor is

\[ F_{i\eta} = \left\{ \sin^2 \theta_j \cos 2\eta_j \right\} \]  

(2.12)
where $\theta_j$ and $\eta_j$ are the polar and azimuthal angles of the $j$-th axis within the structural unit with respect to the bulk axes, which may relate the biaxial orientation of the structural units to the dichroic orientation factors. These authors show how the Hermans and Stein uniaxial and biaxial orientation factors represent higher order orientation factor terms in the expansion. However, Stein’s biaxial orientation factors and their extensions by Nomura, Kawai and coworkers had a basic problem that the specification of orientation based on the Eulerian angles are prejudiced in favor of a single specific direction in the material, which does not easily express the relative biaxial character of films.

White and Spruiell [129] proposed another approach in 1981, using the relationship between second order tensor of the polarizability and the second moment of the orientation distribution as a guide in defining the most convenient forms of orientation functions. For an amorphous polymer, only orientation of the polymer chain has meaning because of rotation about carbon-carbon bonds and averaging over all segments, which leads to the existence of only two different polarizabilities in the system. Therefore, the suggested definitions of two biaxial orientation functions are expressed as

\[
f^*_z = 2\cos^2\phi_{z,z} + \cos^2\phi_{z,y} - 1
\]

\[
f^*_y = 2\cos^2\phi_{y,y} + \cos^2\phi_{y,z} - 1
\]

where $x, y, z$ axes represent the axes of film and $1, 2, 3$ axes of the polymer molecules as shown in Figure 2.1. The White-Spruiell biaxial orientation functions for a crystalline polymer are generally expressed as
where \( \phi_{z,j} \) and \( \phi_{y,j} \) are the angles between the \( j \)-crystallographic axis (\( j = a, b, \) and \( c \)) and the \( z \)- (MD) and \( y \)- (TD) reference directions, respectively. For an orthorhombic unit cell, they are related by the Pythagorean theorem.

\[
\cos^2 \phi_{z,j} + \cos^2 \phi_{y,j} + \cos^2 \phi_{z,j} = 1
\]

(2.17)

\[
\cos^2 \phi_{y,j} + \cos^2 \phi_{y,j} + \cos^2 \phi_{y,j} = 1
\]

(2.18)

The orientation functions above are also presented in terms of graphical representations with all states of orientation lying within an isosceles triangle of \( f^\beta_z \) and \( f^\beta_y \) with isotropic systems located at the origin as shown in Figure 2.2. States of uniaxial orientation with respect to the machine and transverse direction lie along the respective coordinate axes and states of perfect uniaxial orientation are represented by the three apexes of \((1, 0)\) and \((0, 1)\) representing orientations in the plane of the film and \((-1, -1)\) representing orientation perpendicular to the surface. Equal planar orientation is represented by the point \((1/2, 1/2)\) and all points along the base of the triangle represent orientations within the plane. All points on the dotted line, the altitude of the triangle, represents states for which the orientation with respect to the machine and the transverse directions is the same, i. e., equal biaxial orientation.
Figure 2.1 Coordinate system showing the XYZ axes of film and the 1 (chain), 2, 3 axes of the polymer molecules.

Figure 2.2 Graphical representation of orientation, the orientation triangle diagram.
2.4.2 Measurement of Orientation

The orientation levels of polymer chains or crystallographic axes in oriented samples are commonly characterized by wide angle X-ray diffraction (WAXD), birefringence, and infrared (IR) dichroism.

2.4.2.1 Birefringence

Orientation measurement through birefringence method utilizes the relationship between the refractive index, $n$, and the molecular polarizability, $\alpha$. For an isotropic material, the Lorentz-Lorenz equation describes the relationship as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha}{3}$$

(2.19)

where $N$ represents the number of molecules per unit volume. Provided that Eq. (20) remains valid along the principal axes of the polarizabilities and refractive indices for an anisotropic oriented polymer, the Lorentz-Lorenz relationship may be modified to

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{N\alpha_i}{3}$$

(2.20)

where the $n_i$ is the refractive index and the $\alpha_i$ is the molecular polarizability along the $i$ principal axis. Then, the relationship between the components of the polarizability tensor, $\alpha_{ij}$ and the intrinsic birefringence, $\Delta^o\left(=n_{ii} - n_{\perp}\right)$ maybe expressed as

$$\frac{\alpha_i - \alpha_j}{\alpha_{ii} - \alpha_{\perp}} = \frac{n_i - n_j}{\Delta^o}$$

(2.21)

where
\[
\Delta^o = \frac{1}{18} N \left( \frac{n^* + 2}{n} \right)^2 (\alpha_\parallel - \alpha_\perp)
\] (2.22)

where \( n^* \) represents a mean birefringence and \((\alpha_\parallel - \alpha_\perp)\) the difference in principal polarizabilities along and perpendicular to the polymer chain.

Stein and his coworkers [124,125] criticized the use of previous procedure and its application of the Lorentz-Lorenz equation and have considered the problem where the isotropic assumptions of the Lorentz-Lorenz equation are removed, by using a cylindrical cavity as opposed to the spherical cavity originally used by Lorentz [124].

For amorphous materials, the Hermans uniaxial orientation factor is related to the birefringence through [130]

\[
f_{\parallel} = \frac{3 \cos^2 \phi - 1}{2} = \frac{n_x - n_y}{\Delta^o} = \frac{n_z - n_x}{\Delta^o}
\] (2.23)

and the White-Spruiell biaxial orientation factors are given by the birefringences as [129]

\[
f_{z}^B = 2 \cos^2 \phi_{z} + \cos^2 \phi_{y} - 1 = \frac{n_x - n_y}{\Delta^o}
\] (2.24)

\[
f_{y}^B = 2 \cos^2 \phi_{y} + \cos^2 \phi_{z} - 1 = \frac{n_y - n_x}{\Delta^o}
\] (2.25)

where \(x, y, z\) axes represent the axes of film and \(1, 2, 3\) axes of the polymer molecules as shown in Figure 2.1.

The development of orientation factor above was presumed for single-phase, amorphous materials. For multi-phase, semicrystalline polymers, birefringence contributions from both phases should be introduced with form birefringence. For uniaxial orientation [124],

37
\[ \Delta n = X f_c \Delta_c^o + (1 - X) f_{am} \Delta_{am}^o + \Delta_{form} \]  

(2.26)

where \( \Delta n \) is the in-plane birefringence, \( X \) the crystalline fraction, \( f_c \) and \( f_{am} \) the Hermans orientation factor for the crystalline phase and for the amorphous phase, \( \Delta_c^o \) and \( \Delta_{am}^o \) the intrinsic birefringence for the crystalline phase and for the amorphous phase, respectively, and \( \Delta_{form} \) is the form birefringence. Form birefringence is usually negligible, unless there exists anisotropic distribution of optically isotropic inclusions such as voids. For biaxial orientation [129], the birefringence in a partially crystalline film may be also expressed as the sum of the birefringences of the individual phases plus the form birefringence as

\[
\Delta n_{xx} = X \left[ \Delta_{cb}^c f_{xx}^{Bc} + \Delta_{ab}^c f_{xx}^{Bc} \right] + (1 - X) \Delta_{aa} f_{z_{Ba}} + \Delta_{form} \]  

(2.27)

\[
\Delta n_{yy} = X \left[ \Delta_{cb}^a f_{yy}^{Bc} + \Delta_{ab}^a f_{yy}^{Bc} \right] + (1 - X) \Delta_{aa} f_{y_{Ba}} + \Delta_{form} \]  

(2.28)

where \( \Delta_{cb}^c \) and \( \Delta_{ab}^c \) are the \( cb \)- and \( ab \)-crystallographic direction intrinsic birefringences for the crystalline phases (\( c \)-crystallographic axis as the direction of polymer chains), \( \Delta_{aa} \) the intrinsic birefringence for the amorphous phase, \( f_{z_{Ba}}^{Bc} \) and \( f_{y_{Ba}}^{Bc} \) the orientation factors for the corresponding crystallographic axes, and \( f_{z_{Ba}}^{Ba} \) and \( f_{y_{Ba}}^{Ba} \) are the orientation factors for the amorphous phase.

2.4.2.2 Wide Angle X-ray Diffraction (WAXD)

Pole figures were first developed and applied by Sisson [122] to polymers (cellulose) in an effort to quantitatively measure orientation determined by X-ray diffraction and represent orientation of crystallographic axes in polymers. Afterwards, it became possible to determine and specify the 3-dimensional orientation distribution of
the crystals in a polycrystalline sample. Orientation measurements for semicrystalline polymers are today commonly presented through the preparation of pole figures, which are stereographic projections of the diffracted intensities of the poles (normal) to a specific set of crystallographic planes [127,131]. If a normal to a diffracting plane \((hkl)\) intersects a point, \(P\) on a sphere shown in Figure 2.3, the second moment of the orientation distribution can be determined from the pole figure constructed for this plane as

\[
\frac{\cos^2 \phi_{hkl,z}}{\int_0^{2\pi} \int_0^{\pi} I_{hkl}(\phi, \beta) \sin \phi \cos \phi \, d\beta \, d\phi} = \frac{\int_0^{2\pi} \int_0^{\pi} I_{hkl}(\phi, \beta) \sin \phi \, d\beta \, d\phi}{\int_0^{2\pi} \int_0^{\pi} I_{hkl}(\phi, \beta) \sin \phi \, d\beta \, d\phi}
\]  

(2.29)
where $I_{hkl}$ is the distribution of the diffracted intensity from the $(hkl)$ planes in the pole figure, and $\phi$ and $\beta$ are the spherical coordinates shown schematically in Figure 2.3. Pole figures may be also used to determine the biaxial orientation factors of crystallographic axes using Eqs. (2.15) and (2.16).

2.4.2.3 Infrared Dichroism

Birefringence measures mean values over all the components and phases present, whereas the infrared dichroism technique is specific to particular absorption bands. Therefore, local orientations from different groups on the same molecule, different segments in a copolymer, or different components of a polymer blend can be measured by dichroism. Infrared (IR) dichroism utilizes the anisotropic absorption of electromagnetic waves associated with a certain atomic vibration in oriented polymer samples. This anisotropy is studied with a linearly polarized incoming light and the simplest representation is by the dichroic ratio

$$D = \frac{A_\parallel}{A_\perp}$$

(2.30)

where $A_\parallel$ and $A_\perp$ are the absorbances when the polarization direction of the electric vector of the incoming wave is parallel and perpendicular to the stretching direction, respectively. Therefore, the dichroic ratio becomes zero for isotropic systems.

Fraser [132] developed the IR dichroism method for the orientation measurement in the polymer systems. For uniaxial orientation factor,

$$f_{u1} = \frac{D - 1}{D + 2} \cdot \frac{D^* + 2}{D^* - 1} , \quad D^* = 2 \cot^2 \alpha$$

(2.31)
where $D^o$ is the dichroic ratio when the chain axes are perfectly oriented with the stretching direction and related to the angle, $\alpha$ which represents the angles between transition-moment vector and electric vector of incoming, linearly polarized electromagnetic waves. It was first applied to uniaxially oriented polyethylene by Stein and Norris [124]. For biaxial orientation, IR dichroism was related the White-Spruiell orientation factors through [133]

$$\frac{A_{11} - A_{33}}{A_{11} + A_{22} + A_{33}} = \frac{D_{13} - 1}{D_{13} + D_{23} + 1} = f_1^B \frac{D^o - 1}{D^o + 2}$$

$$\frac{A_{22} - A_{33}}{A_{11} + A_{22} + A_{33}} = \frac{D_{23} - 1}{D_{13} + D_{23} + 1} = f_2^B \frac{D^o - 1}{D^o + 2}$$

(2.32) (2.33)

2.5 Kinematics, Dynamics and Heat Balance in Injection Molding

Polymer melts experience a complicated thermo-mechanical history during the injection molding process, where the molding cycle, consisting of filling, packing and cooling stages, which are programmed to be repeated automatically. In screw injection molding, polymer pellets are plasticated in a single-screw extruder, and a specified amount of molten polymer accumulates at the tip of the screw in a reservoir. The melt is, then, pushed forward by the screw whose displacement is controlled by hydraulic pressure. The melt flows through the nozzle, which connects the extruder to the mold, passes through the sprue, along the runner, through the gate, and into the mold cavity. The melt enters the mold cavity where it begins to solidify as it touches the mold wall. As polymer melts solidify, they shrink as a result of densification. Pressure is maintained during the packing and cooling stages in order to ensure that additional melt continues to
flow into the mold. Once solidification is complete, the mold plates open and the part is ejected.

In order to understand structure development in injection molding process, it is necessary to numerically solve most of the problems since the physical nature of the polymer melt flow during this process exhibits three-dimensional non-isothermal and non-Newtonian properties. There have been various attempts to simulate the melt flow and heat transfer by numerous investigators [134-137]. With considerations limited to one-dimensional shear flow, the continuity, momentum and energy equations describing the injection molding process are of forms, respectively as shown below [137].

\[
\frac{\partial \rho}{\partial t} + v_1 \frac{\partial \rho}{\partial x_1} = -\rho \frac{\partial v_1}{\partial x_1} \tag{2.34}
\]

\[-\frac{\partial p}{\partial x_1} + \frac{\partial}{\partial x_2} \left( \eta \frac{\partial v_1}{\partial x_2} \right) = 0 \tag{2.35}
\]

\[
\rho C_p \left( \frac{\partial T}{\partial t} + v_1 \frac{\partial T}{\partial x_1} \right) = k \left( \frac{\partial^2 T}{\partial x_2^2} \right) + \sigma_{12} \left( \frac{\partial v_1}{\partial x_2} \right) + \rho \Delta H X \left( \frac{\partial X}{\partial t} + v_1 \frac{\partial X}{\partial x_1} \right) \tag{2.36}
\]

where \( \rho \) is density, \( C_p \) heat capacity, \( T \) is temperature, \( t \) is time, \( v_1 \) flow direction velocity, \( x_1 \) flow direction, \( x_2 \) the direction normal to the part surface, \( k \) thermal conductivity, \( \sigma_{12} \) shear stress, \( \Delta H \) the heat of crystallization and \( X \) is crystalline fraction.

2.6 Structure Development of Various Polyolefins in Injection Molding

There exist structural heterogeneities in thick parts of polymeric products such as injection molded articles, where their characteristics have been found to be a strong function of the level of orientation and crystallinity, which vary from the surface to the
core of the molded part. These structural heterogeneities are caused by a complicated thermo-mechanical history of the polymer melt, which is invoked by material properties, mold and delivery system geometries, and molding conditions. Studies on the development of microstructures, especially from orientation and crystallinity, in injection molded polyolefins and also amorphous polystyrene are reviewed.

2.6.1 Atactic Polystyrene

We begin with atactic polystyrene which is a prototype vitrifying polymer. When amorphous glassy polymers are injection molded, the flow-induced shear and normal stresses develop during the mold filling and lead to molecular orientation. During the subsequent cooling stage, these stresses do not completely relax and appear as frozen-in birefringence in the vitrified molded amorphous polymer. Frozen-in orientation and residual stresses also develop from the non-equilibrium density or shrinkage change of the polymer during the inhomogeneous rapid cooling through the glass transition temperature [138-140].

In the early 1950’s, Spencer and Gilmore [141,142] made first investigations on the molecular orientation and residual stresses of injection molded glassy polystyrene parts, pressure losses and fluid mechanics of the mold filling and flow visualization of the filling process.

A decade Later, Ballman, Jackson and Toor [134,143,144] performed the pioneering study of orientation development during injection mold filling and they found that dog-eared birefringence profiles in thin injection molded sections. Specifically, little birefringence in the center of the part was found with maximum birefringence at
intermediate positions. Ballman and Toor [144] proposed that this orientation distribution is the result of a solid layer along the mold wall, a linear shear stress distribution in the flowing melt and a fountain like motion at the front which deposits hot melt from the center of the mold onto the wall where it solidifies.

Menges et al. [145,146] found that the molecular orientation in the direction of flow is highest at the subskin and also the skin layers and close to zero at the center of the molding. They proposed that polymer chains possess high molecular orientation at the skin layer owing to the elongational flow at the advancing front and these chains immediately freeze, preserving their orientation in the flow direction as they reach the cold mold wall. Wales et al. [147-149] also published various papers on injection molding of polystyrene, focusing on experimental studies on the verification of the stress-optical rules in polymer melts through birefringence measurements on rheometric flow of polymers and on injection molded parts. Kamal and Tan [150] agreed by observing the presence of two maximum birefringence peaks near the external surfaces of the mold and a low value in the center. They proposed that the first minimum of the birefringence between these two maxima is associated with the instantaneous freezing of the melt at the mold wall and the second maximum in the subskin layer is attributed to the thickness of the frozen layer at the end of the filling process.

There also have been considerable efforts to predict orientation distribution in injection molded polystyrene by several researchers [135,139,151-153]. The issue is as described by Dietz and White [139], orientation as represented by birefringence
determined by the Rheo-Optical rule and is associated with normal and shear stresses
during mold filling and their subsequent partial relaxation.

2.6.2 Polyethylene

In injection molding of semicrystalline polymers, much more complicated
structures are developed by a complex interaction between orientation and crystallization
phenomena. The morphology and orientation distribution of injection-molded PE in the
depth direction of the mold has been studied by numerous investigators [154-158].

It has been generally found that injection-molded PE parts possess the Bunn
orthorhombic crystal structure throughout the cross-sections and has been proposed
[156,157,159] that four distinct layers can characterize the crystalline morphology in the
thickness direction. The first, skin layer exhibited a non-spherulitic structure with tiny
slots of vertical bright lines arranged in rows, running parallel to the surface of the
molding when viewed in longitudinal cross section. Such a row structure in the skin layer
was interpreted as stacks of lamellae with the chain axis oriented in the flow direction
with growing in the depth direction. Very fine asymmetric spherulites were observed in
the second layer and their size were almost uniform since the size of spherulites was
limited by very fast nucleation rate from larger undercooling. The third layer contained
asymmetric oblate spherulites with axis of symmetry in the depth direction and randomly
nucleated spherulites growing in all directions were observed in fourth layer.

Tan and Kamal [157] related the distribution of morphological layers and
orientation in PE to the processing conditions of the molding operation and to the thermal
history of the flowing melt by taking into account aspects of crystallization kinetics. They
found that increasing the inlet melt temperature decreased the thickness of the non-spherulitic skin layer, while the thickness of the fine asymmetric, spherulitic second layer decreased with the increase in the mold temperature. Spherulite sizes were found to increase in moving toward the core of the mold except when additional melt altered the crystallization process in the packing stage of the mold operation.

Heise et al. [154,160], Heckmann et al. [155], Kamal et al. [156,161] and more recently Wu and White [158] described the orientation distribution of injection-molded PE through its thickness direction in terms of orientation factor and wide angle X-ray diffraction pole figure studies. It has been found that the level of orientation is well developed in the surface and decreased with approach to the core of the mold. The general behavior of crystalline orientation indicated that a $b$-axis orientation, which is the crystal growth direction, is perpendicular to the flow and width directions, while $a$- and $c$-crystallographic axes are in a plane parallel to the mold wall. With higher stress levels during the mold filling, untwisted lamellar structures were found to develop, suggesting that $c$-, $a$-, and $b$-crystallographic axes should correspond to the flow, width and thickness directions, respectively. It was also found that the surface region of the mold showed to some extent the asymmetric X-ray intensity distribution in the plane of the flow and thickness directions with respect to the flow direction, which indicates that the flow direction is not always parallel to the major principal axis of the crystalline orientation.
2.6.3 Isotactic Polypropylene

Structure development in injection molding PP has been studied by numerous researchers and it is also well known that the injection molded PP parts consist of heterogeneous microstructures.

Kantz et al. [162], who published the first study, concluded that there were three layers of heterogeneous microstructures in injection molded PP parts by optical microscopy and X-ray diffraction techniques. A highly oriented, non-spherulitic structure was found in the skin layer and row- or shear-nucleated spherulites were observed in the intermediate layer called transition layer of shish-kebab structure with well-defined spherulitic core layer of low orientation. He found that all of three layers were highly crystalline and the spherulites in the transition zone are bunched tightly together along thin, negatively birefringent rows. He observed that the thickness of the former layer is a function of melt temperature and varies inversely with it, while the transition layer thickness varies with injection pressure. Increases in the sum of the skin and transition layer thickness resulted in improved mechanical properties such as yield strength, impact strength and shrinkage.

Clark [163] reviewed the results of Kantz et al. [162] and proposed that the skin can be interpreted as the portion crystallized during the filling stage where a large number of fibrillar nuclei are formed and lamellar overgrowths have a planar habit under the high stress of elongational flow, whereas the lateral extent of the lamella may be greater in the transition zone with few fibrils present than under high stress and these structures can appear as oblate spherulites with their short axes parallel to injection direction.
Table 2.2 Distinct layers from injection molded PP parts

<table>
<thead>
<tr>
<th>Layer</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Fine grain structure</td>
</tr>
<tr>
<td>II</td>
<td>a. Fine spherulites</td>
</tr>
<tr>
<td></td>
<td>b. Texture showing preferred orientation</td>
</tr>
<tr>
<td></td>
<td>c. Fibrous transcrystalline material</td>
</tr>
<tr>
<td>III</td>
<td>Core: Random orientation with two types of spherulites</td>
</tr>
</tbody>
</table>

Fitchmun and Mencik [164,165] carried out further investigations and argued the microstructure consisted of five layers in injection molded PP parts. Menges et al. [166] also reported the five-layered morphology as described in Table 2.2.

A parent-daughter or a bimodal orientation model from epitaxial lamellar branching described in Section 2.2.2.1, has been suggested to characterize the lamellar structure near the surface of the injection molded PP parts [167-170]. The parent and the daughter lamellae can be linked by tie molecules along the flow direction, but the parent and the daughter lamellae have quite different but related $c$-axis orientations. The parent lamellae have folding chains with their $c$-axis preferentially aligned along the flow direction while the daughter lamellae have their $a'$-axis (originated by $a$-axis of the daughter lamellae) parallel to the $c$-axis of the parent lamellae, having epitaxially grown from the parent. Compared with the parent lamellae, the daughter lamellae are small and imperfect, and the size of daughter lamellae is not uniform. The $b$-axis of the parent lamellae is parallel to the $b$-axis of the daughter lamellae, and the tilt angle between the parent and daughter lamellae is found to be $80^\circ$ [55,76].
Polymorphic crystal structures of monoclinic $\alpha$- and hexagonal $\beta$-crystalline forms varying with injection molding conditions and sample position have been reported by several studies [137,171,172]. Trotignon et al. [171] reported that variations in the degree of crystallinity, molecular orientation induced by non-isothermal flow on crystallization, and the relative amount of $\beta$-crystalline forms are related to a complex layered microstructure of PP moldings. They found that a strong orientation, owing to high stresses and high cooling rates, favors the hexagonal $\beta$-phase crystallites, which is in a good agreement with later researchers [137,172] who found that the monoclinic $\alpha$-form dominates in the skin layer and the core while there exists a mixed structure of the monoclinic $\alpha$- and the hexagonal $\beta$-crystalline forms in the layers between them.

2.6.4 Isotactic Polybutene-1

Bowman et al. [173] investigated the mechanical behavior of the injection molded PB1 to identify the influence of the preferred orientation on properties. They reported that the molded parts exhibited higher crystallinity and density level in the skin layer than those in the core part. They also examined the influence of processing conditions on structure distribution. The thickness of the highly oriented skin layer decreased with increases in either the inlet melt or the mold temperature, and higher skin density was obtained from higher molecular weight PB1 than from lower one, which was attributed to the higher level of orientation owing to the increased relaxation times.

A decade later in the early 1990’s, Lee and Chen [174] confirmed the results of Bowman et al. [173] and investigated the more detailed morphological features by use of polarized light optical microscopy (PLOM) and scanning electron microscopy (SEM).
They observed three distinct regions in the injection molded PB1. The outmost region from the mold was the skin layer, consisted of almost dull or featureless outer band and inner band of many compact tiny bright lines almost perpendicular to the mold surface. The formation of oblate spherulites with their short axes parallel to the injection direction was observed in the transition layer, followed by the typical spherulitic core.

More recently, Kalay et al. [175,176] compared the effect on the structure of PB1 between shear-controlled orientation injection molding (SCORIM) and conventional injection molding. In a conventional injection molding, they observed the similar morphologies by earlier investigators [173,174] except that one additional zone of a fairly broad featureless oriented zone was formed between the transition and the core region when PB1 was processed under higher packing pressure. In SCORIM, where the application of macroscopic shear stress produces more pronounced molecular alignment that leads to increased orientation in the resulting microstructure, interlocking shish-kebab morphology was observed in the shear-influenced regions of the moldings. They reported that PB1 processed either by conventional injection molding or SCORIM at high packing pressure exhibited crystal modifications of Form I as well as Form I’, which is also stable form and has a much lower melting point of 96 °C with the same X-ray diffraction pattern as Form I.

2.6.5 Isotactic Poly(4-methyl pentene-1)

Owen and Hull [177] investigated the microstructure of injection molded P4MP1. They divided the molded part into five sub-layers of different arrangements of crystal lamellae. The first layer from the mold surface exhibited perpendicular lamellae to the
surface and injection direction. The maximum birefringence was observed with lamellae approximately parallel to the injection direction and the surface in the second layer, which was followed by the third layer where the lamellae are oriented in a similar way to those in the first layer at angles between 60° and 80° to the surface and the injection direction. The core of the molded part was divided into the fourth and fifth layers. The former consisted of lamellae with orientation similar to that in the second layer while the lamellae were perpendicular to the mold surface, twisting about the thickness direction of the part in the fifth layer.

Subsequently, Bevis et al. [178,179] reported similar five layers of different level of orientation by investigating the effect of injection pressure, inlet melt and mold temperatures on the microstructures. They reported that the variations in the positions and the extents of these regions were a strong function of inlet melt temperature, compared with mold temperature and the investigated injection pressure, both of which had little effect. They also observed that (200) pole figure exhibited a single crystal texture from the layer of the highest orientation in the injection molded specimen processed at the inlet melt and mold temperatures of 300 °C and 20 °C with the injection pressure of 68 MN/m².
CHAPTER III
EXPERIMENTAL

3.1 Introduction

The main purpose of this study is to determine and develop comparative understanding of variations in structure development of various polyolefins in the injection molding process in a quantitative manner.

Rheological properties and crystallization kinetics of raw materials were determined and related to final micro-structures in the molded part. The molded part microstructure was characterized, focusing on the crystallinity, orientation, crystal structure and micro-morphology development as a function of thickness direction of the molded part. This was measured by experimental techniques such as polarized optical micrographs, birefringence, wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). The effect of processing variables was also investigated by changing injection pressure, injection speed, packing pressure, mold temperature and inlet melt temperature.

3.2 Materials

Four different types of semicrystalline polyolefins were used in this study. The effect of side group in the repeating unit of semicrystalline polyolefins on crystallization and orientation during the injection molding process was investigated. The polymers used
included high-density polyethylene (PE), isotactic polypropylene (PP), isotactic polybutene-1 (PB1) and isotactic poly(4-methyl pentene-1) (P4MP1). In an effort to consider the effect of nucleating agents, two grades of PB1 were included. One of PB1 grade (PB1N) was nucleated with a small amount of high density polyethylene (HDPE) [180]. Atactic polystyrene (a-PS) was also used in this study to compare between crystalline and amorphous materials. The characteristics of these polymers are tabulated as shown in Table 3.1. The polymers are all injection molding grades.

Table 3.1 List of materials used in this study

<table>
<thead>
<tr>
<th>Material (Identification)</th>
<th>Melting* Temp. (°C)</th>
<th>Density (g/cm³)</th>
<th>Melt Flow Rate (g/10min)</th>
<th>Resin Provider &amp; Commercial Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-PS (PS)</td>
<td>(T₀ ~ 100 °C)</td>
<td>1.04</td>
<td>14 (200 °C, 5.0 kg)</td>
<td>Dow Chemical Inc. &amp; Styron 615APR</td>
</tr>
<tr>
<td>PE (PE)</td>
<td>131</td>
<td>0.965</td>
<td>30 (190 °C, 2.16 kg)</td>
<td>Equistar Chemicals. &amp; Alathon® H6030</td>
</tr>
<tr>
<td>PP (PP)</td>
<td>161</td>
<td>0.90</td>
<td>5.0 (230 °C, 2.16 kg)</td>
<td>Equistar Chemicals. &amp; Petrothene® PP8001LK</td>
</tr>
<tr>
<td>PB1 (PB1)</td>
<td>110</td>
<td>0.915</td>
<td>1.8 (190 °C, 2.16 kg)</td>
<td>Basell &amp; PB200</td>
</tr>
<tr>
<td>PB1 (PB1N)</td>
<td>113</td>
<td>0.915</td>
<td>0.4 (190 °C, 2.16 kg)</td>
<td>Basell &amp; PB0110</td>
</tr>
<tr>
<td>P4MP1 (P4MP1)</td>
<td>224</td>
<td>0.834</td>
<td>26 (260 °C, 5.0 kg)</td>
<td>Mitsui Chemical Inc. &amp; TPX® MX004</td>
</tr>
</tbody>
</table>

*Melting temperatures were measured with methods mentioned in Section 3.3.1.

3.3 Material Characterization Methods

Basic properties of raw materials supplied by various provide were characterized, which include thermal properties, crystallization kinetics, rheological properties, and
molecular weight and its distributions. In the following sections, detailed experimental techniques and procedures are described.

3.3.1 Melting Temperature and Crystallinity

The melting temperatures and crystallinities of semicrystalline polyolefins are to be measured by using a Perkin-Elmer differential scanning calorimetry (DSC) purged with nitrogen gas. Each material was placed in a DSC pan with a weight of 5 mg approximately and heated up to 200 °C (291 °C for P4MP1). After staying three minutes in the heated temperatures to erase any processing history, samples was cooled down to a room temperature at the rate of 10 °C/min and reheated at the rate of 10 °C/min. From the crystalline melting peak observed during this heating, the crystalline melting point and crystallinity were determined from the peak position and peak area, respectively.

3.3.2 Crystallization Kinetics

The isothermal and non-isothermal quiescent crystallization rates were investigated using a Perkin-Elmer DSC. The melts were cooled down from 200 °C (291 °C for P4MP1) to a room temperature at various cooling rates (1 °C/min ~ 40 °C/min) for non-isothermal crystallization rate measurements. Continuous cooling transformation (CCT) curves were constructed from the crystallization onset temperature and the corresponding elapsed time, which is the time required for crystallinity to reach 100 % of final crystallinity from the crystallization onset temperature.

In isothermal crystallization kinetic studies, the melts were subject to a rapid quenching to a specific crystallization temperature and then stay at the temperature until
the crystallization becomes complete. Crystallization half-time \((t_{1/2})\), the time required for the crystallinity to reach 50 % of final crystallinity, were plotted against corresponding crystallization temperature. All measurements were carried out in a nitrogen atmosphere with a connected intercooler to make sure of stable thermal control.

3.3.3 Shear Viscosity

The steady laminar shear viscosities of all materials were measured at the melt temperatures of 180, 200 and 220 °C except P4MP1 because of its high melting point. For the latter polymer, the viscosity was measured from 240 to 291 °C. The viscosities at low shear rates, from 0.01 s\(^{-1}\) to 10 s\(^{-1}\), were obtained from steady rate sweep using the ARES (Advanced Rheometric Expansion System) of Rheometric Scientific Inc., with a cone-plate apparatus of dimensions 25 mm diameter and cone angle 0.1 radian. The viscosities at high shear rates over 10 s\(^{-1}\) to 10\(^3\) s\(^{-1}\) were obtained using an Instron capillary rheometer with three dies of L/D equal to 9.3, 19.3, and 28.5 mm, where barrel and die diameters are 9.5 and 1.6 mm, respectively. We applied standard viscometric calculation procedures such as the Bagley plot to eliminate ends pressure loss and the Weissenberg correction for the die wall shear rate.

In the geometry of a cone-plate rheometer, the shear rate, which becomes nearly uniform through the gap with a small angle of a cone, can be expressed as

\[
\dot{\gamma} = \frac{\Omega}{\tan \alpha} \approx \frac{\Omega}{\alpha}
\]  

(3.1)
where $\Omega$ is angular velocity and $\alpha$ is the cone angle. The shear viscosity, $\eta$, can be obtained from the shear stress, $\sigma$, which is determined by the amount of torque applied, as

$$\sigma = \frac{3M}{2\pi R^3} \quad (3.2)$$

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{3M}{2\pi R^3} \frac{\alpha}{\Omega} \quad (3.3)$$

where $M$ is the torque and $R$ is the cone radius.

In the capillary rheometry, the wall shear rate is expressed through the Weissenberg relationship as

$$\dot{\gamma}_w = \dot{\gamma}_a \left[ 3 + \frac{d \ln \dot{\gamma}_a}{d \ln \sigma_R} \right] \quad (3.4)$$

where $\dot{\gamma}_a$ is the apparent wall shear rate and $\sigma_R$ is the wall shear stress, which are expressed as

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (3.5)$$

$$\sigma_R = \left( \frac{-dp}{dz} \right) \frac{R}{2} \quad (3.6)$$

where $Q$ is the volumetric flow rate, $R$ the die radius, and $dp/dz$ is the pressure gradient in the capillary, which is usually approximated by $-\Delta P/L$ for a Newtonian fluid, where $\Delta P$ is the pressure drop across the whole capillary including the entrance and $L$ is the capillary length. The pressure gradient for polymeric materials, however, is nonlinear and should be modified by considering the entrance pressure drop, $\Delta P_{\text{ent}}$ and the exit pressure drop,
\( \Delta P_{\text{ex}} \), the total of which is called the ends pressure, \( \Delta P_{\text{end}} \). The true wall shear stress is obtained as

\[
\sigma_R = \left( \frac{\Delta P_{\text{tot}} - \Delta P_{\text{end}}}{L} \right) \frac{R}{2}
\]  

(3.7)

The shear stress can also be corrected by calculating the equivalent die length required to produce, \( \Delta P_{\text{tot}} \) and expressed with \((L/D)_c\), the corrected value of \(L/D\) [181]. The true wall shear stress, \( \sigma_R \) is now given as

\[
\sigma_R = \frac{\Delta P_{\text{tot}}}{(L/D)_c} / 4
\]  

(3.8)

3.3.4 Stress Relaxation

Stress relaxation measurements of polyolefin melts were performed by the step strain experiment using ARES under isothermal conditions for comparison of time required of materials to relax after deformation. The parallel plate configuration was used with the diameter of 25 mm and the gap of 1.8 mm. The relaxation modulus, \( G(t) \) was recorded by examining the material response to a step shear strain. The magnitude of step strain was 2% at 200 °C for all materials except P4MP1, where it was 291 °C. During these experiments, nitrogen gas was purged to prevent oxidative degradation. Prior to the application of the step strain, the linear viscoelastic range was determined by strain sweep experiment and the specimen between two disks was relaxed at the targeted temperature until it doesn’t exhibit a normal force associated with the loading.
3.3.5 Molecular Weight and Molecular Weight Distribution

Efforts to estimate molecular weights ($M_w$) and molecular weight distributions ($\text{PDI} = M_w/M_n$) from rheological properties were made, based on the correlations made by White et al. [182,183]. They found that the magnitude of the zero shear viscosity, $\eta_o$ is determined by the absolute molecular weight and the rate of decrease of $\eta/\eta_o$ increases with molecular weight distribution breadth, when $\eta/\eta_o$ was plotted as a function of $\eta_o\dot{\gamma}$, as reported by Vinogradov and Malkin [184]. The zero shear viscosity was measured at the shear rate of $10^{-2}$ s$^{-1}$ and the relative breadth of molecular weight distributions was compared at $\eta_o\dot{\gamma} = 10^6$ Pa$^{-1}$.

3.4 Injection Molding Procedure

A reciprocating screw injection molding machine, Van Dorn 55 HP was used in this study to prepare injection molded specimens, of which shape is rectangular with dimensions of $127 \times 12.7 \times 3.18$ mm. Several series of injection molding experiments

<table>
<thead>
<tr>
<th>Materials</th>
<th>Melting Points ($T_m$, °C)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-PS (PS)</td>
<td>$T_g \sim 100$ °C</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>PE (PE)</td>
<td>131</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>PP (PP)</td>
<td>161</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>PB1 (PB1)</td>
<td>110</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>PB1 (PB1N)</td>
<td>113</td>
<td>200</td>
<td>43</td>
</tr>
<tr>
<td>P4MP1 (P4MP1)</td>
<td>224</td>
<td>291</td>
<td>43</td>
</tr>
</tbody>
</table>
were carried out with constant injection pressures (65.5 MPa) or volumetric injection speeds, Q, ranging from 5.38 cm$^3$/sec to 53.76 cm$^3$/sec, and two packing pressures, 10 and 70 MPa, which were applied for 10 seconds.

The thermal conditions of injection molding were divided into two different categories as shown in Table 3.2. In the category noted as A, the melt and mold temperatures were maintained at the same absolute value, 200 °C and 43 °C, except for the melt temperature of P4MP1 (291 °C) where this is not possible. In category B, the differences between the melt temperatures and the melting points and between the melting points and the mold temperatures were kept constant at 67 °C and 70 °C for all the semicrystalline polyolefins. 30 seconds of cooling time was given to all molded parts.

3.5 Structural Characterization

Samples from different position and depth in the molded part were prepared by using Reichert HistoSTAT rotary microtome in order to investigate the structural heterogeneities as a function of thickness direction. For birefringence measurements and polarized optical micrographs, a layer of 50 µm thickness (~ 1mm for PS) was obtained from the middle of the molded part as shown in Figure 3.1, where MD stands for the machine, flow direction, ND for the normal, thickness direction, and TD for the transverse, width direction in the molded part, respectively. 50 µm thick layers were microtomed from the surface to the core of the molded part for X-ray diffraction investigations.
3.5.1 Birefringence and Polarized Optical Micrographs

The birefringence of the samples prepared from each injection molded article was determined as a function of position using a Leitz polarized optical microscope (Leitz Laborlux 12Pol) with 4- and 30-order Berek tilting compensators. When polarized light passes through a specimen in the parallel direction to the transverse direction (TD) as shown in Figure 3.1, a phase difference develops between two components of a wave vector along direction 1 (MD) and 2 (ND). A zero phase difference can be obtained by tilting the compensator to a certain angle and a dark extinction line is observed at this position. Then, the birefringence is calculated as

$$\Delta n_{12} = \frac{\Gamma}{d}$$

(3.9)

where $\Gamma$ is the optical retardation and $d$ is the layer thickness. The values of retardation along the thickness direction of the layer was measured by following the extinction lines and corresponding birefringence values were plotted against the normalized distance, $z/H$, of which value is zero at the mold surface and 1 at the very core.
The crystalline morphology of each layer (~20µm along A-cut) was also investigated through optical photomicrographs using crossed polarizers in a Leitz optical microscope. Sizes and ranges of structural entities were measured with rotating samples under crossed polarizers.

3.5.2 WAXD Investigations

Crystal structure and the level of crystalline orientation in polyolefin molded parts were mainly investigated by Wide Angle X-ray Diffraction (WAXD) techniques. The middle of the molded part was microtomed and description of structure variation was carried out as a function of depth from the surface of the mold. The total 32 layers from the surface to the core of the molded part were obtained with 50 µm thickness each using microtoming procedures described in Figure 3.1. The first 8 layers from the surface (0 < z/H < 0.25) were investigated individually and numbers were assigned from #1 to #8 for those layers with #1 representing the layer at the very surface. As approaching to the core, we combined 2 layers (#9~#16 corresponding 0.25 < z/H < 0.5) and 4 layers (#17~#32 corresponding 0.5 < z/H < 1) together, where the layer of #32 is located at the very core of the mold, since less variation of orientation has been observed in deeper region of the molded part in birefringence measurements.

3.5.2.1 WAXD Film Patterns

Wide angle X-ray diffraction (WAXD) film patterns were obtained using a GADDS (General Area Detector Diffraction System) by Bruker AXS, Inc., which is equipped with Bruker AXS HI-STAR 2D area detector and a CuKα radiation of 1.5418
Å wavelength and a flat graphite monochromator. 40 kV and 40 mA of operation voltage and current were used on the layers of the molded parts prepared according to Figure 3.1. Sample to detector distance was kept constant at 11.5 cm and a collimator of 0.8 mm diameter was used for typical qualitative analysis, texture, or percent crystallinity measurements. The 2D area detector, at 11.5 cm distance from the sample, could only capture diffraction image around 35% of whole diffraction pattern. We used 25% of whole diffraction pattern, which, as long as it contains equatorial and meridional lines of the pattern, can represent all the information necessary to study crystalline structure owing to symmetric nature of X-ray diffraction onto the film. Each sample was mounted and set in the sample holder such that the incident X-ray beam is perpendicular to the machine, flow and transverse, width directions and parallel to the normal, thickness direction of the sample.

3.5.2.2 WAXD $\theta$ Scans

After capturing a WAXD film pattern for a certain layer by use of Bruker X-ray machine, corresponding $\theta$ scan spectrum for the layer was also obtained. Compared with a scintillation detector where necessary scan is limited to small spot or a position sensitive detector (PSD), which is capable of simultaneous large $\theta$ scan only, it was possible to obtain large range of $\theta$ and azimuthal angle, $\chi$ for the Debye-Scherrer cone simultaneously in much shorter time with Bruker 2-D area detector. Each $\theta$ scan was made in the range of $5^\circ \leq \theta \leq 40^\circ$ and $0^\circ$ (equatorial) $\leq \beta \leq 90^\circ$ (meridional).
3.5.2.3 WAXD Pole Figures

A 3-dimensional description of the state of crystalline orientation in oriented samples as a function of thickness in the mold was determined by using a WAXD pole figure measurements in GE-XRD 6, which is equipped with a CuKα radiation (1.5418 Å) and a graphite monochromator. The diffraction intensities were recorded at every 5° increments of azimuthal angle, φ and every 10° increments of rotation angle, β for 30 seconds under operation voltage and current of 30 kV and 30 mA, respectively.

Out of 32 total layers from the surface to the core of the molded articles, samples from a certain depth (#1, #3, #5, #7, #9–#10, #13–#14, #17–#20, and #25–#28) were prepared by stacking several pieces of the same B-cut layers such that its dimension becomes 1.0 × 1.0 × 12.0 mm. They were mounted on the diffractometer with its machine, flow direction parallel to the principal reference direction, the sample rotation axis.

For PE, pole intensities from (110) and (200) crystallographic planes were measured according to the procedure mentioned above. For PP, we measured the spatial distribution of (110) and (040) crystallographic planes from α-monoclinic structure. We needed to investigate pole figures from 2 crystallographic planes in the cases of an orthorhombic unit cell of PE and a monoclinic unit cell of PP, in order to calculate biaxial orientation factors. Spatial variation of pole intensities from only a single crystallographic plane was necessary for biaxial orientation factor calculations of PB1 and P4MPI due to their hexagonal and tetragonal unit cell characteristics, respectively.

Stereographic projections from 3-dimensional pole intensity data were prepared by using a surface mapping software, Surfer32 from Golden Software, Inc. The MD-, ND-,
or TD-centered pole figures were constructed through a coordinate transformation, and biaxial orientation factors were calculated and compared.

3.5.3 Crystallinity in Fabricated Parts

The crystallinity level of layers, which were microtomed from the molded parts as shown in Figure 3.1, were measured by a Perkin-Elmer DSC. Each layer was put in the DSC pan and heated from atmospheric temperature to the temperature below which melting of crystalline fractions is completed. A heating rate of 50 °C/min was applied to ca. 5 mg of specimen in order to achieve metastable state, where recrystallization of an oriented sample during heating is prevented. The levels of crystallinities, which were determined by the ratio of crystalline melting peak area to the generally accepted 100 % crystalline heat of fusion, $\Delta H_m^0$, were plotted against the normalized distance from the mold surface, $z/H$. 
4.1 Introduction

Understanding the characteristics of the basic polymers used in this dissertation is important from the perspectives not only in set-up of proper processing conditions, but also in evaluations and analysis of resulting structure developed in the fabricated parts. In this chapter, we present the characteristics of the polymer physical properties through experimental techniques described in the previous chapter.

4.2 Results

Basic properties of raw materials characterized are described in the following sections, which include melting behavior and crystallinity, isothermal and non-isothermal crystallization kinetics, and rheological behaviors including shear viscosity and stress relaxation behavior.

4.2.1 Melting Temperature and Crystallinity

Differential scanning calorimetry (DSC) heating scans showing the melting behavior of the as-received polyolefins are shown in Figure 4.1. Melting temperatures and crystallinities of polyolefins provided from various companies were measured through DSC heating scans according to the procedure described earlier in Section 3.3.1.
Melting temperature determined from the peak and crystallinity calculated from the area of each polyolefin’s heating thermogram are listed in Table 4.1. Based on the melting temperatures obtained, thermal conditions for injection molding were established to provide equivalent thermal history. It seems that all polyolefins studied exhibit fairly high

![Figure 4.1 DSC heating of the as-received polyolefins at 10 °C/min scanning rate](image)

**Table 4.1 Melting temperature and crystallinity of raw polyolefins through DSC scans**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Melting Points ($T_m$, °C)</th>
<th>$\Delta H_{exp}$ (J/g)</th>
<th>$\Delta H^o$ (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE (PE)</td>
<td>131</td>
<td>208</td>
<td>277 [185]</td>
<td>75</td>
</tr>
<tr>
<td>PP (PP)</td>
<td>161</td>
<td>77</td>
<td>138 [186]</td>
<td>56</td>
</tr>
<tr>
<td>PB1 (PB1)</td>
<td>110</td>
<td>48</td>
<td>126 [187]</td>
<td>38</td>
</tr>
<tr>
<td>PB1 (PB1N)</td>
<td>113</td>
<td>64</td>
<td>126 [187]</td>
<td>51</td>
</tr>
<tr>
<td>P4MP1 (P4MP1)</td>
<td>224</td>
<td>26</td>
<td>52 [188]</td>
<td>50</td>
</tr>
</tbody>
</table>
level of crystallinity, confirming these polyolefins lie in the category of fast crystallizing polymers. The heat of fusion values for 100% crystalline polyolefins were selected from published values in the literature [185-188].

4.2.2 Crystallization Kinetics

Overall crystallization rates of polyolefins were investigated under both isothermal and non-isothermal conditions through DSC scans and we sought to describe relative crystallization rates of various polyolefins.

\[ \Delta T = T_m - T_c \]

Figure 4.2 Plots of crystallization half-times as a function of supercooling for the various polyolefins.

In isothermal crystallization kinetics, the crystallization half-time, \( t_{1/2} \), which is defined as the time required for relative crystallinity, \( X(t) \) to reach 50\% of its final crystallinity. In Figure 4.2, the crystallization half-time is plotted in a logarithmic scale as a function of supercooling, calculated from the difference between specific crystallization
temperature and equilibrium melting temperature of each polymer. The equilibrium crystalline melting temperature from the Polymer Handbook [189] was selected as 135 °C for polyethylene, 165 °C for isotactic polypropylene, 126 °C for the crystal Form II of isotactic polybutene-1, which is known to be kinetically favored [35,190] and 235 °C for isotactic poly(4-methyl pentene-1).

The relative crystallization rates among the four polyolefins investigated may be determined through relative positions and slopes with supercooling from Figure 4.2, where PB1N shows increased crystallization rate due to the effect of nucleating agent. Considering non-nucleated polyolefins, it seems that the ranking of polymers in terms of decreasing crystallization rate would be

\[ PE > P4MP1 > PP > PB1 \]  \hspace{1cm} (4.1)

It is notable that the crystallization rate of P4MP1 is comparable with that of PE even though it has a bulky side group, which may create steric hindrance. The validity of supercooling as crystallization rate comparison would be maintained as long as there is no delayed nucleation [191].

We have also studied rates of crystallization following steady rates of cooling and this allows us to obtain continuous cooling transformation (CCT) curves, originally used by metallurgists for steel [192,193] and later applied to polymers [194,195]. In CCT curves shown in Figure 4.3, the difference between the equilibrium melting temperature and the crystallization onset temperature, was plotted as a function of logarithmic elapsed time. We are able to compare relative rates of crystallization for different polymers. From
Figure 4.3, we may conclude that the behavior orders as same as Eq. (4.1) which summarized observations in the isothermal case.

![Continuous Cooling Transformation (CCT) curves of various polyolefins](image)

Figure 4.3 Continuous Cooling Transformation (CCT) curves of various polyolefins

4.2.3 Shear Viscosity

The relative flow property quoted by material manufacturers is usually MFR (Melt Flow Rate) and is limited in a sense that MFR only represents the extrusion rate under a specific condition such as a single pressure and temperature. In order to better understand flow behavior under deformation, it is necessary to investigate rheological behavior more extensively.
Shear melt viscosities were determined as described in Section 3.3.3. They are plotted at 200 °C (291 °C for P4MP1) as a function of shear rate in Figure 4.4. In the low shear rate region, relative order of shear viscosities are as follows.

$$PB1N > PP \sim PB1 > PS > P4MP1 \sim PE$$  \hspace{1cm} (4.2)

As shear rate increases, polymer melt experiences large shear thinning and non-Newtonian properties. PP and PB1N show a fast decrease of viscosity with increase of shear rates, while PS show the least shear thinning. Around a shear rate of $10^3$ s$^{-1}$, the relative order of shear viscosity is as follows.

$$PB1 \sim PS > PE \sim PP \sim PB1N \sim P4MP1$$  \hspace{1cm} (4.3)
4.2.4 Stress Relaxation

In shear stress relaxation experiment described in Section 3.3.4, the molten sample is held between two parallel disks under isothermal conditions. Upon a sudden introduction of the shear strain $\gamma$, which is imposed at time $t=0$ by applying a large and measured by the time decay of the shear stress, $\sigma(t, \gamma)$ through:

$$G(t, \gamma) = \frac{\sigma(t, \gamma)}{\gamma}$$  \hspace{1cm} (4.4)

We chose to use 2% step strain for the stress relaxation tests which we found to be in the linear response range.

Figure 4.5 Shear stress relaxation following 2% step strain for polyolefin melts at 200 °C (291 °C for P4MP1)

The relaxation moduli are plotted as a function of the time of relaxation in Figure 4.5. The relaxation moduli of PE and P4MP1 decrease much faster than most of other polyolefins, while PP and PB1N show slower relaxation. It should be noted that the
relative order of stress relaxation time is similar to the order of the shear viscosity at low shear rates. The stress relaxation behavior was used to interpret the orientation observed in injection molded parts.

4.3 Interpretation

In this section, we make interpretations of our experimental results on the crystallization kinetics and rheological properties with comparing them with those in the literature.

4.3.1 Crystallization Kinetics

Crystallization kinetics of polyolefins used in this study are compared with earlier studies of these polymers as well as those of other hydrocarbons.

4.3.1.1 Comparison to Earlier Studies of These Polymers

We first sought comparison of our results with the earlier literature. Generally for the polymers studied, the rates of crystallization observed are very similar to those reported in the literature. Griffith and Ranby [42] made dilatometric measurements on crystallization rate of P4MP1 and compared it with those of PE, PP and PB1. It was found that the crystallization rate of P4MP1 is slower than that of PE and faster than those of PP and PB1. Silvestre et al. [104] also carried out an isothermal crystallization study of P4MP1. The results of Silvestre et al. are in good agreement with our results, confirming the order of crystallization rates among these polyolefins.
4.3.1.2 Comparison to Other Isotactic Polyhydrocarbons

![Chemical structures](image)

Figure 4.6 Structural units of isotactic (a): polyolefins with linear alkyl side group (b): polyolefins with a branched methyl side group (c): polystyrene

There have been several investigations of crystallization kinetics of other isotactic polyhydrocarbons (compare Figure 4.6). These include polypentene-1 (PPT1) \((n=2)\) [196-198], polyhexene-1 (PH1) \((n=3)\) [199], poly(3-methyl butene-1) (P3MB1) \((m=0)\) [198,200], and polystyrene (PS) [201,202]. If we first limit ourselves to polyolefins with linear alkyl side groups shown in Figure 4.6(a), it is clear from our observations and those of Quinn and Powers [196], Turner-Jones [199], and Dunham et al. [198], that crystallization rates order as

\[
PP \; (n=0) > PB1 \; (n=1) > PPT1 \; (n=2) > PH1 \; (n=3)
\]  

(4.5)

Crystallization rate of course depends on temperature but it seems clear that the ordering of Eq.(4.5) is valid at the same \(T_m - T\) or \(T - T_g\).

It may be argued that introduction of linear side groups causes steric hindrance during crystallization. With a longer side group, the chain comes to possess enhanced mobility and flexibility, which is reflected in a decrease of the glass transition temperatures from PP to PH1 or from P3MB1 to poly(5-methyl hexane-1) (P5MH1) as
shown in Table 4.2, where helical conformations and crystalline density with glass transition and crystalline melting temperatures of various polyolefins are summarized from the literature [189].

Table 4.2 Physical properties of various isotactic polyolefins with linear polyethylene

<table>
<thead>
<tr>
<th>Samples</th>
<th>Conformation</th>
<th>Density^# (g/cm^3)</th>
<th>Crystallization Rates</th>
<th>T_g/T_m (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Planar zigzag</td>
<td>1.00</td>
<td>Very fast</td>
<td>-83/135</td>
</tr>
<tr>
<td>PP</td>
<td>3_1</td>
<td>0.94</td>
<td>Fast</td>
<td>-10/165</td>
</tr>
<tr>
<td>PB1</td>
<td>11_3</td>
<td>0.90</td>
<td>Medium</td>
<td>-35/126</td>
</tr>
<tr>
<td>PPT1</td>
<td>3_1</td>
<td>0.87</td>
<td>Slow</td>
<td>-40/75</td>
</tr>
<tr>
<td>PH1</td>
<td>7_2</td>
<td>0.73</td>
<td>Difficultly crystallizable*</td>
<td>-55/-</td>
</tr>
<tr>
<td>P3MB1</td>
<td>4_1</td>
<td>0.93</td>
<td>Fast</td>
<td>94/300</td>
</tr>
<tr>
<td>P4MP1</td>
<td>7_2</td>
<td>0.83</td>
<td>Fast</td>
<td>29/235</td>
</tr>
<tr>
<td>P5MH1</td>
<td>3_1</td>
<td>0.84</td>
<td>Slow</td>
<td>-14/130</td>
</tr>
<tr>
<td>PS</td>
<td>3_1</td>
<td>1.13</td>
<td>Very slow</td>
<td>100/240</td>
</tr>
</tbody>
</table>

#: Density from crystalline phase
*: Crystallizable to a few percent only under stretch

Up to linear propyl side-chain branching in case of PPT1 (n=2), main chains of a helical conformation were considered to be incorporated into crystallites by side-by-side packing of themselves by Quinn et al. [196] and Danusso et al [196,197]. They reported that PPT1 crystallizes isothermally with a maximum crystallization rate at 26 °C, and although it crystallizes to a fairly high degree, its crystallization rate is much slower than those of PE, PP and PB1. With a longer side chain, the side-by-side packing of helices presumably becomes more and more open, which can also be conjectured from crystalline density decrease. This more open packing would result in difficulties for both main and side chains to form a regular three dimensional network. It is likely, when considering the very low density of the monoclinic unit cell of PH1, which was only found to crystallize under stretch at -20 °C (by Turner-Jones [199]), that the changeover
of crystallization behavior from the main chain crystallization to side-chain crystallization may start to occur in PH1 when we consider that crystallization in isotactic polyolefins with longer side groups than that of PH1 have been argued to take place mainly between side chains instead of main chains as concluded in earlier investigations [199,203,204].

Turning to the few studies of the crystallization of polyolefins with linear alkyl side group with methyl branches shown in Figure 4.6(b), we find that these polymers seem to crystallize quite rapidly. This is the conclusion we must reach from Dunham et al. [198] and Kirshenbaum et al. [200] for the case of $m=0$ (P3MB1) and our own work and that of Lopez et al. [103] and Silvestre et al. [104] for $m=1$ (P4MP1). Crystallization in long chains of helical conformation has been known to take place when adjacent isotactic helices approach each other with opposite rotations, allowing two chains to be locked to each other through van der Waals forces between side chains. Introduction of additional methyl group decreases the degree of flexibility of side chain, which can be related with the increase in melting temperatures from decrease in the entropy of fusion, and favors its positioning for van der Waals bonding. It seems that a better balance between flexibility and bulkiness of side chain for crystallization would be achieved in P3MB1 or P4MP1 than in PP. As the bulky portion of side chain moves away from the vicinity of side chain, melting temperature and crystallization rate decrease due to increased flexibility of the side chain as observed in the case of $m=2$, poly(5-methyl hexane-1) (P5MH1) [205,206].

There have also been studies of the crystallization of isotactic polystyrene [201,202], of which chemical structure is shown in Figure 4.6(c). These studies indicate
that isotactic polystyrene crystallizes very slowly compared to those of the isotactic polymers described above. The increase in crystallization rates from PB1 to P3MB1 and PPT1 to P4MP1 seems to become possible with limited chain flexibility from the introduction of methyl group. In the case of isotactic polystyrene, however, the substituent phenyl group must create too much crowding and consequently ends up with very slow crystallization.

4.3.1.3 Avrami Interpretation

With the assumption that the development of crystallinity is proportional to the amount of heat released during the process of crystallization, the relative degree of crystallinity, $X(t)$ can be described as

$$X(t) = \frac{\int_0^t (dH_c / dt) dt}{\int_0^\infty (dH_c / dt) dt}$$ (4.6)

where $dH_c$ is the rate of heat evolution during an infinitesimal time interval $dt$. The time limits, $t$ and $\infty$, correspond to the elapsed time during the course of crystallization and at the end of crystallization process, respectively. The increases of crystallinity level with time for the polyolefins investigated under isothermal conditions are shown in Figure 4.7, where we plot the logarithm of $[-\ln{1-X(t)}]$ versus the logarithm of time.

It can be seen that well-defined straight lines are obtained at several crystallization temperatures for each of the polyolefins with deviation from linearity in the region close to the beginning and the end of crystallization. This is probably attributable to the characteristics from initial nucleation and secondary crystallization processes. The individual isotherms can be brought into together by shifting each curve along the
Figure 4.7 Plots of log [-ln{1-X(t)}] as a function of log t for isothermally crystallized polyolefins (a: PE, b: PP, c: PB1, d: P4MP1)

horizontal axis, and as the crystallization temperature is increased, isotherms move to the right along the horizontal axis, indicating that the crystallization rate becomes slower. This suggests that crystallization rate data involves the concurrence of nucleation and growth processes [207].

Isothermal crystallization kinetics is generally interpreted in terms of the kinetic model of Johnson and Mehl [208] and Avrami [209] which has the form

\[
\frac{dX}{dt} = N(t)(1 - X) \tag{4.7}
\]

where N is the crystallization rate constant. Eq.(4.7) may be solved to give
\[ X(t) = 1 - \exp(-kt^n) \]  
\hspace{1cm} (4.8)

For homogeneous nucleation, the Avrami exponent equals 4 for three-dimensional linear crystal growth, \( n = 3 \) and \( n = 2 \) for two- and one-dimensional growth, respectively. For heterogeneous nucleation, \( n \) represents the dimensionality of the crystal growth. The overall crystallization rate analysis from Figure 4.7 still shows good adherence to the Avrami equation and we compare the results of the Avrami analysis in the present study with those values from early investigators.

Table 4.3 Values of crystallization half-time, \( t_{1/2} \), Avrami exponent and crystallization rate parameter, \( n \) and \( k \) at different crystallization temperatures, \( T_c \) for various polyolefins

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_c ) (°C)</th>
<th>( t_{1/2} ) (min)</th>
<th>( n )</th>
<th>( k ) (min(^{-n}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>118</td>
<td>1.79</td>
<td>2.33</td>
<td>1.79 x 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>119</td>
<td>3.87</td>
<td>2.36</td>
<td>2.85 x 10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>8.00</td>
<td>2.39</td>
<td>4.79 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>121</td>
<td>19.17</td>
<td>2.79</td>
<td>1.84 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>53.90</td>
<td>2.76</td>
<td>1.14 x 10(^{-5})</td>
</tr>
<tr>
<td>PP</td>
<td>121</td>
<td>2.63</td>
<td>2.34</td>
<td>7.19 x 10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>5.51</td>
<td>2.60</td>
<td>8.22 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>127</td>
<td>15.13</td>
<td>2.49</td>
<td>8.06 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>129</td>
<td>25.07</td>
<td>2.53</td>
<td>1.98 x 10(^{-4})</td>
</tr>
<tr>
<td></td>
<td>131</td>
<td>36.56</td>
<td>2.51</td>
<td>8.31 x 10(^{-5})</td>
</tr>
<tr>
<td>PB1</td>
<td>72</td>
<td>2.41</td>
<td>2.59</td>
<td>7.11 x 10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>76</td>
<td>4.04</td>
<td>2.60</td>
<td>1.83 x 10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>6.42</td>
<td>2.69</td>
<td>4.64 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>8.94</td>
<td>2.44</td>
<td>3.29 x 10(^{-3})</td>
</tr>
<tr>
<td></td>
<td>84</td>
<td>11.19</td>
<td>2.43</td>
<td>1.98 x 10(^{-3})</td>
</tr>
<tr>
<td>P4MP1</td>
<td>216</td>
<td>1.11</td>
<td>1.92</td>
<td>5.70 x 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>217</td>
<td>1.55</td>
<td>1.89</td>
<td>3.04 x 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>2.24</td>
<td>1.92</td>
<td>1.47 x 10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>5.33</td>
<td>1.65</td>
<td>4.37 x 10(^{-2})</td>
</tr>
<tr>
<td></td>
<td>221</td>
<td>8.95</td>
<td>1.64</td>
<td>1.90 x 10(^{-2})</td>
</tr>
</tbody>
</table>
We determined fractional Avrami exponents for the various polyolefins investigated in this study as shown in Table 4.3. Fractional values of Avrami exponents and deviation of experimental data especially at long crystallization times have been known as major problems of analyzing experimental data [210]. The experimentally derived kinetic parameters based on the Avrami equation, however, can represent experimental data conveniently as long as there is a good agreement between theory and experimental data, such as well-defined Avrami plots and kinetic parameters shown in Figure 4.7 and Table 4.3, respectively. We found the Avrami exponents between 2 and 3 for all polyolefins except P4MP1, which showed a lower value close to 2. Silvestre et al. [104] argued that Avrami exponent of 2, which is similar to what we obtained in our own Avrami analysis, describes the crystallization process of P4MP1 better than n = 4 reported by Griffith and Ranby [42] and Yadav et al. [102]. The range of values for Avrami exponents of the materials of this study are reported in Table 4.4. For the most part, the values are in the same range as our data.

Table 4.4 Avrami exponents of polyolefins of this study reported in the literature

<table>
<thead>
<tr>
<th>Samples</th>
<th>Earlier Reported $n$</th>
<th>Ref.</th>
<th>Our values of $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>2–4</td>
<td>[90], [211]</td>
<td>2.33–2.79</td>
</tr>
<tr>
<td>PP</td>
<td>3–4, 1.8–3.2</td>
<td>[212], [97]</td>
<td>2.34–2.60</td>
</tr>
<tr>
<td>PB1</td>
<td>2–3, 3, 4</td>
<td>[81], [213], [214], [98]</td>
<td>2.43–2.69</td>
</tr>
<tr>
<td>P4MP1</td>
<td>2, 3, 4</td>
<td>[104], [102], [42]</td>
<td>1.64–1.92</td>
</tr>
</tbody>
</table>
4.3.2 Rheological Characteristics

Information on the molecular weight of the materials was obtained from the providing companies for PB1, P4MP1 and PS in Table 4.5. Estimation of molecular weights of those materials, of which information was not available (PE and PP), was carried out using the shear viscosity data we have measured and is shown in Figure 4.4. The molecular weights of linear polyethylene and isotactic polypropylene could be estimated using correlations with zero shear viscosities by Münstedt et al [215,216]. They found correlation of the zero shear viscosity of linear polyethylene with the weight average molecular weight [215] as

\[ \eta_0(Pa \cdot s) = K \cdot M_w^\alpha \text{ where } K=9 \times 10^{-13}, \alpha=3.6 \text{ at } 150^\circ C \]  

(4.9)

and for isotactic polypropylene [216],

\[ \eta_0(Pa \cdot s) = K \cdot M_w^\alpha \text{ where } K=4 \times 10^{-16}, \alpha=3.5 \text{ at } 180^\circ C \]  

(4.10)

The temperature dependence of zero shear viscosity should be considered and it can be represented with shift factor, \( a_T \), which is calculated using an Arrhenius equation.

\[ a_T = \frac{\eta_T}{\eta_o} = \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right] \]  

(4.11)

With flow activation energies, \( E_a \) of 6.4 kcal/mole and 10.0 kcal/mole for linear polyethylene and isotactic polypropylene, respectively [217], Eq.(4.9) and Eq.(4.10) have been adjusted to 200 °C and expressed in logarithmic forms as

\[ \log \eta_o(Pa \cdot s \text{ at } 200^\circ C) = -14.4 + 3.6 \log M_w \text{ for linear polyethylene} \]

\[ \log \eta_o(Pa \cdot s \text{ at } 200^\circ C) = -15.6 + 3.5 \log M_w \text{ for isotactic polypropylene} \]  

(4.12)
Through zero shear viscosities measured at the shear rate of $10^{-2}$ s$^{-1}$ from Figure 4.4, estimations of weight average molecular weights of PE and PP was made. These are listed in Table 4.5 with molecular weight information on PB1, P4MP1 and PS provided by the suppliers.

![Figure 4.8 The Vinogradov-Malkin plots for polyolefin melts](image)

Figure 4.8 The Vinogradov-Malkin plots for polyolefin melts

Number average molecular weights of PE and PP can also be estimated form molecular weight distribution (MWD), which can be predicted in a qualitative manner by using the Vinogradov-Malkin plot [184] as shown in Figure 4.8. It has been found with the Vinogradov-Malkin plot that with broader MWD, the ratio of viscosity to zero shear viscosity, $\eta / \eta_0$, decreases faster as $\eta_0 \dot{\gamma}$ increases. Comparing the relative shear thinning behaviors of PE and PP with other polyolefins of which MWDs were already known, the relative breadth of MWD of PE and PP was estimated through $\eta / \eta_0$ measured at $\eta_0 \dot{\gamma} = 10^6 Pa$ [182,183]. It seems that PP possesses the most broad MWD
comparable with that of PB1N and PS shows fairly narrow distribution. Other polyolefins, including PE, PB1 and P4MP1, exhibit MWDs around 5, which is in between two groups of polyolefins mentioned above.

Table 4.5 Molecular weight and molecular weight distribution of polyolefins

<table>
<thead>
<tr>
<th>Materials</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE (PE)</td>
<td>$\sim1.02 \times 10^4$</td>
<td>$5.10 \times 10^4$</td>
<td>$\sim5$</td>
</tr>
<tr>
<td>PP (PP)</td>
<td>$\sim5.84 \times 10^4$</td>
<td>$4.09 \times 10^5$</td>
<td>$\sim7$</td>
</tr>
<tr>
<td>PB1 (PB1)</td>
<td>$1.07 \times 10^5$</td>
<td>$5.25 \times 10^5$</td>
<td>$4.9$</td>
</tr>
<tr>
<td>PB1 (PB1N)</td>
<td>$1.29 \times 10^5$</td>
<td>$8.55 \times 10^5$</td>
<td>$6.6$</td>
</tr>
<tr>
<td>P4MP1 (P4MP1)</td>
<td>$1.20 \times 10^5$</td>
<td>$6.00 \times 10^5$</td>
<td>$5.0$</td>
</tr>
<tr>
<td>$\alpha$-PS (PS)</td>
<td>$8.96 \times 10^4$</td>
<td>$1.85 \times 10^5$</td>
<td>$2.1$</td>
</tr>
</tbody>
</table>

4.4 Conclusions

The characteristics of the raw polymer materials of interest were investigated in this chapter. This mainly concerned crystallization and rheological behaviors.

We investigated the comparative crystallization rates of various polyolefins under both isothermal and non-isothermal crystallization conditions. It is particularly interesting to observe under both conditions the order of relative crystallization rates from fast to slow one as: $PE > P4MP1 > PP > PB1$. It is notable that the crystallization rate of P4MP1 is faster than that of PP, even though P4MP1 possesses a bulkier side group, which may create larger steric hindrance effect for longer and bulkier molecular chains to be incorporated into crystalline region. This unusual fast crystallization rate of isotactic P4MP1 is perhaps due to the loose packing nature of the 7/2 helical chain conformation, combined with unique density feature of this polymer, which shows a bit lower density.
from crystalline phase (0.83 g/cm\(^3\)) than from amorphous phase (0.84 g/cm\(^3\)) at ambient temperature [42,43]. It has been well known that polyolefins possess isotropic melts above its melting temperature. There, however, have been some studies suggesting the possibility of long-range order in the P4MP1 melt [218,219], which may promote crystallization and could be another explanation for faster crystallization. Except for P4MP1 and earlier studies of P3MB1, the comparative rates of crystallization seem to be in agreement with bulkiness of side groups in a sense that the bulkier side group would provide larger steric hindrance to chain folding, resulting in slower crystallization rate. An Avrami kinetic analysis of these polyolefins was carried out. This indicated good agreement with theory and earlier results. An Avrami equation with exponent slightly less than the value of 2 was found for P4MP1 in our study.

Zero shear viscosities were used to estimate \(M_w\) as shown in Table 4.5 and the relative breadth of molecular weight distribution (\(M_w/M_n\)) among various polyolefins were compared by using the Vinogradov-Malkin plot and we found out that the distribution broadens as follows.

\[
PS(\sim 2) < PE, PB1, P4MP1(\sim 5) < PB1N(6.6) < PP(\sim 7)
\]  

(4.13)
5.1 Introduction

In this chapter, we describe the structure development of polyolefins in injection molding, which were processed under several volumetric injection rates. By investigating birefringence, crystallinity and WAXD patterns of internal layers from the surface to the core of molded parts, we have been able to evaluate the level of structure developed in each individual polymer under a certain processing condition and describe the effect of processing parameters as well. We look at the influence of volumetric injection rate, packing pressure, mold and inlet melt temperatures, using methods described in Section 3.4.

Crystal structure and possible polymorphism, which may occur with different processing conditions for the various polyolefins, are investigated through WAXD 2θ scans while qualitative crystalline orientation development is studied by observing WAXD film patterns as a function of depth in molded articles.

5.2 Results

Characterizations among various polyolefins injection molded under four different injection volumetric flow rates, two packing pressures and two thermal conditions are
described in the following sections through birefringence, WAXD and crystallinity measurements.

5.2.1 Birefringence

The average molecular orientation contributed by both amorphous and crystalline regions as well as volumetric quench effects can be described through birefringence measurements. The levels of birefringence in injection molded polyolefin parts were investigated in micromted samples with a cross polarized optical microscope with a Berek compensator. The procedures for sample preparation and techniques for measurement are described in Section 3.5.1.

The birefringence profiles of molded polyolefins including amorphous polystyrene are plotted as a function of depth from the surface to the core of the mold from Figure 5.1 to Figure 5.5. Four different volumetric injection rates (from 5.38 cm$^3$/sec to 53.76 cm$^3$/sec) were applied with two packing pressures (10 MPa and 70 MPa) and two thermal conditions (A and B). We determined $\Delta n_{12}$ values for layer through the cross-sections of the molded parts, where ‘1’ stands for machine, flow direction and ‘2’ for normal, thickness direction, respectively. Along the horizontal axis in these plots, the normalized distance from the surface of the mold is shown with ‘0’ indicating the surface and ‘1’ indicating the core of the molded part. The skin and transition layer thickness, which can be defined as the width from the mold surface to the first peak and second peak of birefringence profile, were investigated as well as the relative magnitude of birefringence values in those layers in various polyolefins. The resulting birefringence was also correlated to the effect of processing parameters.
5.2.1.1 Atactic Polystyrene

Figure 5.1 shows birefringence profiles of atactic polystyrene (PS) injection molded at 200 °C of inlet melt temperature, $T_{\text{melt}}$ and 43 °C of mold temperature, $T_{\text{mold}}$ (thermal condition, A), with various injection rates ranging from 5.38 cm$^3$/sec to 53.76 cm$^3$/sec. Results from two different packing pressures, 10 MPa and 70 MPa, are shown in Figure 5.1 a) and b), respectively.

![Figure 5.1](image_url)

**Figure 5.1** Birefringence profile as a function of depth from the surface to the core of injection molded PS (Styron® 615APR) at different processing conditions

It can be seen in both plots that the injection molded PS parts show negative birefringence values throughout the whole depth of the mold. Birefringence generally exhibits high values in the region close to the mold wall and decreases toward the middle of the molded part. As injection rate increases, birefringence increases in the skin and transition layers with its values from $-0.002$ to $-0.005$. The minima between the first maximum and second peaks of birefringence profile move closer to the mold wall with increase of injection rates as well as second peaks. These minima eventually disappear at
the highest injection rate, 53.76 cm³/sec, and birefringence profile shows monotonic decrease from the surface to the core of the mold, except another increase in the middle of the molded parts, which have been processed using higher packing pressure. The width of skin and transition layers decreases from 0.12 to 0.03 with increase of injection rates.

The tendency for birefringence to decrease from the surface to the deeper position changes around the normalized distance of 0.3 in Figure 5.1 b), where higher packing pressure was applied, while there is no discernible birefringence after this distance in Figure 5.1 a), where lower packing pressure was used. The molded parts from higher packing pressure show rather broad peaks in the middle of the part. The maximum reached is ca. – 0.0014 with slight tendency of decrease with increase of injection rates.

5.2.1.2 Polyethylene

Birefringence profiles of high density polyethylene (PE) are shown in Figure 5.2. Four injection rates and two different packing pressures were applied to the molded parts with thermal condition, A (T_melt = 200 °C & T_mold = 43 °C) and thermal condition, B (T_melt = 198 °C & T_mold = 61 °C).

In Figure 5.2, there seem three well-defined sublayers which might be described as skin layer, transition layer and the core region. In each plot from different processing conditions, the birefringence profiles exhibit very high gradients in the skin layer toward the thickness direction, showing the highest values at the mold surface. The highest values ranges from 0.013 to 0.020, which increases with increase of injection rates. The next transition layers also show quite high birefringence levels from 0.009 to 0.015,
Figure 5.2 Birefringence profile as a function of depth from the surface to the core of injection molded PE (Alathon® H6030) at different processing conditions which also increase with injection rates. Passing though the transition layers, birefringence decreases fast toward the core region. In the region deeper than the normalized distance of 0.3, birefringence of the molded parts under lower packing pressure, 10 MPa, is very low around 0.005, while the application of higher packing pressure, 70 MPa, results in additional and rather broad peaks with maxima around 0.010 in the middle of the molded parts.
The skin and transition layers move closer to the mold wall with increase of injection rates. It is also found that increase of mold temperatures from 43 °C in thermal condition, A to 61 °C in thermal condition, B shifts the location of skin and transition layers toward the mold surface with slight decrease in the level of birefringence in the transition layer, while the magnitude of birefringence in the skin layer doesn’t seem to be affected by mold temperature variation in this range.

5.2.1.3 Isotactic Polypropylene

Figure 5.3 shows birefringence profiles of isotactic polypropylene (PP), which were processed varying volumetric injection rates and packing pressures under thermal condition, A (T_{melt} = 200 °C & T_{mold} = 43 °C) and thermal condition, B (T_{melt} = 228 °C & T_{mold} = 91 °C).

The molded PP parts show three sublayers, i.e. the skin and transition layers, and core region. The molded parts have high birefringence values both at the mold surface and the transition layer. The birefringence values at the skin layer ranges from 0.013 to 0.018, showing increase with increase of injection rates. Thickness of the skin layer decreases with increase of injection rates, ranging from 0.12 to 0.03 of the normalized distance from the mold surface.

In the next transition layer, the birefringence shows maximum values higher than those from the skin layer, especially at higher injection rates. They range from 0.009 to 0.023 and the locations of birefringence peaks in the transition layer move closer to the mold wall with increase of injection rates. From Figure 5.3 a) or c) where thermal condition, A (T_{melt} = 200 °C & T_{mold} = 43 °C) was applied, it can be seen that the
Figure 5.3 Birefringence profile as a function of depth from the surface to the core of injection molded PP (Petrothene® PP8001LK) at different processing conditions.

Birefringence maxima in the transition layer decreases from 0.27 down to 0.09 of the normalized thickness distance. With higher melt and mold temperatures in thermal condition, B (T\textsubscript{melt} = 228 °C & T\textsubscript{mold} = 91 °C) applied in the case of Figure 5.3 b) or d), the peaks of the skin layers seem to be combined into the steeply decreasing birefringence curves right at the mold wall. The maxima of the transition layers also make shift toward the mold wall with increase of the inlet melt and mold temperatures.
5.2.1.4 Isotactic Polybutene-1

Birefringence measurements of injection molded isotactic polybutene-1 (PB1N) parts are shown in Figure 5.4, which were processed using various injection rates and packing pressures under thermal condition, A ($T_{melt} = 200 \, ^\circ C$ & $T_{mold} = 43 \, ^\circ C$) and thermal condition, B ($T_{melt} = 180 \, ^\circ C$ & $T_{mold} = 43 \, ^\circ C$).

![Graphs a-d](image_url)

Figure 5.4 Birefringence profile as a function of depth from the surface to the core of injection molded PB1N (Basell PB0110) at different processing conditions
Birefringence profiles of injection molded PB1N parts show the highest values in the skin layer (0.011 ~ 0.017) and gradually decrease down to the transition layer (0.009 ~ 0.013), of which peaks are located between 0.05 and 0.30 of the normalized distance. Passing through the transition layer and moving deeper toward the core region, birefringence decrease rather rapidly and eventually stays at the values around 0.005 or less except slight increase from the molded parts at higher packing pressure. As shown in Figure 5.4 b) and d), it is observed that birefringence maintains high values at deeper position in the thickness direction with lower inlet melt temperature in the case of thermal condition, B (20 °C lower than the case of thermal condition, A).

5.2.1.5 Isotactic Poly(4-methyl pentene-1)

In Figure 5.5, birefringence profiles of injection molded isotactic poly(4-methyl pentene-1) (P4MP1) parts processed under various conditions, which include four injection rates, two packing pressures and two thermal conditions: thermal condition, A (T_melt = 291 °C & T_mold = 43 °C) and thermal condition, B (T_melt = 291 °C & T_mold = 154 °C).

The skin-core birefringence profiles described for the other polyolefins nor any distinguishable micro sublayers are observed in P4MP1. Instead, very low level of birefringence exists all along the depth of the molded parts in different processing conditions. Even though P4MP1 shows little birefringence, it still exhibits the effect of mold temperature variation such that non-zero birefringence values move towards the mold surface with increase from 43 °C to 154 °C (Thermal condition A to B in Figure 5.5). The maximum birefringence value for P4MP1 does not exceed 0.0007.
Figure 5.5 Birefringence profile as a function of depth from the surface to the core of injection molded P4MP1 (TPX® MX004) at different processing conditions

5.2.2 Crystallinity of Fabricated Parts

Crystallinity variations of molded polyolefin parts, as determined by differential scanning calorimetry (DSC) of small sections of parts as described in Section 3.5.3, were investigated. They are shown in Figure 5.6. In the region close to the mold wall, where normalized distance, z/H ranges from 0 to 0.25, crystallinity variation of each polyolefin has a resemblance with birefringence profile, except P4MP1. Starting from z/H = 0.5,
crystallinity increases gradually with approaching to the core region. The relative level of % crystallinity is in order of

\[ PE > PP > PB1 > P4MP1 \]  \hspace{1cm} (5.1)

No appreciable crystallinity was observed in injection molded PS parts.

Figure 5.6 Degree of % crystallinity of polyolefins injection molded under thermal condition: B, injection rate: 35.84 cm$^3$/sec, and packing pressure: 70 MPa (thermal condition, A was used for PS)

5.2.3 WAXD Film Patterns

From Figure 5.7 to Figure 5.10, we show wide angle X-ray Diffraction (WAXD) patterns, with which we could determine crystal structure and qualitative crystalline orientation of polyolefins. With more emphasis on the surface, patterns were taken at sixteen different depths, covering whole range of depth from the surface to the core of the
Our birefringence results showed that structural variation is stronger in the region close to the mold wall than in the inner portion of the mold and more layers were selected for investigation of surface regions of four different set of molded parts. These parts were produced with the injection parameters (a)~(d)). A quarter of whole film pattern was obtained for each layer, which still include all the crystalline information necessary for the study of crystal structure and crystalline orientation owing to symmetric nature of X-ray diffraction onto the film. Layers of interest were mounted in a way that meridional and equatorial lines of the pattern should be correspondent with machine, flow direction (MD) and transverse, width direction (TD), respectively.

5.2.3.1 Atactic Polystyrene

No crystalline structure was observed through WAXD patterns of PS as there was not any appreciable crystallinity.

5.2.3.2 Polyethylene

In Figure 5.7, we could confirm that well-known orthorhombic crystal structure forms in injection molding of high density polyethylene at various processing conditions through observations of strong diffraction peaks from (110) and (200) planes at the \(d\)-spacings of 4.10 Å and 3.70 Å, respectively. Qualitative crystalline orientation from these WAXD patterns shows that the level of orientation is not very high all the way from the surface to the core among the different samples. It is notable that the low level of orientation and little variation among samples are found even though high level of shear stress during mold filling was presumably provided.
5.2.3.3 Isotactic Polypropylene

In case of injection molded isotactic polypropylene (PP) shown in Figure 5.8, it was found through diffraction peaks from the planes of (110), (040) and (130) at 6.26 Å, 5.19 Å and 4.77 Å from α-monoclinic crystal structure and the (300) at 5.51 Å from β-hexagonal unit cell that polymorphism arises. It was observed that the α-monoclinic form is dominant in the skin layer and the core zone, while mixtures of α-monoclinic and β-hexagonal forms exist in the transition layer, where the relative amount of β-hexagonal form seems to depend on the level of shear and thermal stresses applied. The effect of processing conditions on the level of orientation becomes more evident in these patterns.
With the colder mold wall shown in Figure 5.8 a) compared with Figure 5.8 b) or c), orientation penetrates deeper. As injection rate increases from Figure 5.8 b) or c) to Figure 5.8 d), higher orientation moves closer to the mold wall. The WAXD patterns in the skin and transition layers of PP exhibit well oriented structure.

Figure 5.8 WAXD film patterns of PP (Petrothene® PP8001LK): a) 5.38 cm$^3$/sec, 70 MPa, A b) 5.38 cm$^3$/sec, 10 MPa, B c) 5.38 cm$^3$/sec, 70 MPa, B d) 35.84 cm$^3$/sec, 70 MPa, B (injection rate, packing pressure, thermal condition)

5.2.3.4 Isotactic Polybutene-1

Isotactic polybutene-1 (PB1) has been well known to have two major polymorphs from melt crystallization, Form I and Form II (see Section 2.1.3). Form II is formed first and transforms to thermodynamically stable Form I, in time [35,190]. In the present study, the molded PB1 samples were characterized at least two weeks after processing, in order to make sure that there only exists a stable hexagonal Form I, which has strong
Diffraction peaks from the planes of (110), (300) and (220) at 8.85 Å, 5.11 Å and 4.43 Å as found in Figure 5.9. Injection molded PB1N parts show high levels of crystalline orientation in the skin and transition layers and random orientation in the core zone. Even small amount of decrease in inlet melt temperature from 200 °C to 180 °C results in increase of skin and transition layer thicknesses and thus deeper orientation penetration, shown in Figure 5.9 a) and Figure 5.9 c).

Figure 5.9 WAXD film patterns of PB1N (Basell PB0110): a) 5.38 cm³/sec, 70 MPa, A b) 5.38 cm³/sec, 10 MPa, B c) 5.38 cm³/sec, 70 MPa, B d) 35.84 cm³/sec, 70 MPa, B (injection rate, packing pressure, thermal condition)

5.2.3.5 Isotactic Poly(4-methyl pentene-1)

Injection molding of isotactic poly(4-methyl pentene-1) (P4MP1) promotes the most stable crystalline modification, Form I out of the known five different crystalline forms that have been described [220,221] (Section 2.1.4). A tetragonal unit cell of Form I
could be characterized by strong diffraction peaks from the crystal planes of (200) and (220) at 9.33 Å and 6.60 Å as found in Figure 5.10. While PP and PB1N exhibited relatively high crystalline orientation in the skin and transition layers, P4MP1 shows somewhat less level of orientation in all the samples investigated.

![Figure 5.10 WAXD film patterns of P4MP1 (TPX® MX004): a) 5.38 cm³/sec, 70 MPa, A b) 5.38 cm³/sec, 10 MPa, B c) 5.38 cm³/sec, 70 MPa, A d) 35.84 cm³/sec, 70 MPa, B (injection rate, packing pressure, thermal condition)](image)

5.3 Interpretation

In injection molding of polymeric materials, molecular orientation is usually determined by processing parameters coupled with intrinsic material properties. Injection parameters such as injection rate, packing pressure, inlet melt and mold temperatures play important roles in determining microstructure development of final molded parts. Since
this final microstructure is directly related to the properties of products, it is crucial to understand how these parameters affect the level of molecular orientation as a function of thickness of thick molded parts. Total average orientation and qualitative crystalline orientation variations of polyolefin molded parts through birefringence and WAXD techniques allow us to investigate the effect of processing parameters on microscopic orientation development.

5.3.1 Atactic Polystyrene

In the absence of crystallization process, amorphous polymers are vitrified during injection molding process and show rather straightforward results in their structure development. Atactic polystyrene (PS) was used in our study as an amorphous polymer in order to compare its characteristics in orientation development with those of crystalline polyolefins. From crystallinity and WAXD investigations, we could confirm that PS does not possess any appreciable crystalline structure.

Injection molded PS exhibited negative birefringence throughout the cross section of the layer cut from the middle of the molded part, from its intrinsic property that the optical density along the direction of branching is higher than that of main chain direction. As investigated previously by several researchers [143-150], we observed the dog-eared birefringence profile where two maximum birefringence peaks are present close to the mold wall. First peak of birefringence can be interpreted as results from the formation of the frozen layer on the mold wall and the elongational flow at the advancing front. While shear flow-induced orientation results in the second peak of birefringence profile, low
values of birefringence in the middle of the part could be attributed to the longer relaxation time provided in the core region.

5.3.2 Polyethylene

When semicrystalline polymers are injection molded, more complicated structures develop than amorphous polymers, due to a complex interaction between orientation and crystallization phenomena.

Birefringence results of injection molded PE parts from various conditions in Figure 5.2 exhibited maximum values around 0.020, which is in good agreement with previous studies extensively done by Kamal et al. [156,157,159,161]. They reported maximum birefringence up to 0.015 depending on various processing conditions, material properties and locations of interest in the mold. Taking into account of intrinsic birefringence of polyethylene ($\Delta n = 0.057$) [124], the level of orientation of the molded PE parts in the flow direction seems to be somewhat low, equivalent to a Hermans orientation factor of about 0.4. This low level of orientation was confirmed qualitatively through WAXD patterns, which only exhibited the Bunn orthorhombic crystal structures. With considerations of shear viscosity properties of raw materials in Figure 4.4, it could be said that PE melt would experience lower flow stress than other polyolefins during mold filling. It seems that PE would require much higher critical shear rate for highly oriented crystalline structure development due to the characteristics of linear chain conformation in the crystalline region.
5.3.3 Isotactic Polypropylene

Figure 5.11 WAXD $\theta$ scans of PP corresponding diffraction patterns in Figure 5.8

There were three distinct regions consisting of the skin layer, the transition layer and the core region in the birefringence profiles of the injection molded PP parts. This could be correlated to microstructures along the cross section investigated by several researchers [162-166], who in general reported the highly oriented skin layer of fine grain structure, the row structures in the transition layer with high orientation, and the spherulitic core layer of low orientation. In the highly oriented skin and transition layers,
the molded PP parts exhibited as high birefringence as PE, showing maximum values in the vicinity of 0.020. The relative orientation level of PP would be higher than that of PE with consideration of its low intrinsic birefringence ($\Delta^\circ = 0.033$) [222]. This higher level of orientation also could be seen qualitatively through WAXD patterns in Figure 5.8.

From WAXD results, we found polymorphic crystal structures of monoclinic $\alpha$- and hexagonal $\beta$-crystalline forms, of which relative amounts seemed to depend on the molding conditions and positions along the thickness direction of the mold. Figure 5.11 shows WAXD $2\theta$ scans, which correspond diffraction patterns of PP fabricated under different injection conditions (a)–(d)) presented in Figure 5.8. The diffraction peaks at $2\theta$ angle 16.1°, indicated by straight lines, are the (300) reflections of the $\beta$-crystalline form, of which relative amount, $K$ would be estimated through the method of Turner-Jones et al. [21], as

$$K = \frac{H_{\beta 1}}{H_{\beta 1} + (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3})}$$

(5.2)

where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ stand for the heights of three strong reflections of $\alpha$-crystal planes (110), (040) and (130), and $H_{\beta 1}$ the height of the strong single (300) $\beta$-crystalline peak. The relative amount of $\beta$-crystalline form calculated is shown in Figure 5.12 as well as processing conditions. It increases with increase of injection rate from 5.38 cm$^3$/sec to 35.83 cm$^3$/sec as well as the position of maximum moves closer to the mold surface. Both increases in mold and inlet melt temperature from thermal condition A to B also shift the maximum of the curves toward the mold surface. While the effect of
Figure 5.12 Relative amount of $\beta$-crystalline form, $K$, as a function of depth in injection molded PP under shown conditions (thermal condition_injection rate_packing pressure).

Packing pressure is not that evident as other processing parameters, it can be seen that injection molded PP parts have mixtures of $\alpha$-monoclinic and $\beta$-hexagonal crystals in the transition layer and $\alpha$-monoclinic crystal dominant in the skin layer and the core zone. Taking into account orientation results from birefringence and WAXD film patterns, it can be concluded that the formation of the $\beta$-crystal should be promoted with high shearing action in the transition layer, which is in good agreement with previous investigations [171,172].

5.3.4 Isotactic Polybutene-1

A well-defined skin-core morphology was found in injection molded polybutene-1 (PB1N) parts as observed by earlier studies [173,174]. From the birefringence profiles
investigated, the boundary between the skin and transition layers seemed rather flat compared with distinct minimum peaks observed in the moldings of PE and PP. This might be attributed to the high level of shear stress combined with longer relaxation time from the PB1N intrinsic rheological properties as shown in Figure 4.4 and Figure 4.5. Consequently fairly high orientation seems to have developed in the deeper region below the mold surface. The maximum birefringence value \( \Delta_{\text{max}} = 0.017 \) with considerations of the intrinsic birefringence \( \Delta^0_c = 0.02 \), indicates very high orientation, which also could be observed in the WAXD patterns where only Form I was observed throughout all the molding.

5.3.5 Isotactic Poly(4-methyl pentene-1)

We observed well-known dog-eared birefringence profiles for all materials except for P4MP1, which showed very little, almost no birefringence values through the entire region of the mold. Investigations of average orientation in the P4MP1 molded parts through birefringence measurements seemed to be limited because P4MP1 has very low intrinsic birefringence (~ 0.0075) due to almost equivalent polarizabilities \( \alpha_{\parallel} - \alpha_{\perp} \approx 0 \), and optical densities along the main chain and along the substituent group directions [223].

Crystalline orientation development is mainly determined by flow stress, relaxation and crystallization behaviors of the melt during molding filling in injection molding. In our investigations, PP and PB1 exhibited relatively high level of orientation while PE showed lower level of orientation. The relative orientation levels among different
polymers might be ranked according to the critical shear stress for orientation development and helicoidal conformations of PP and PB1 might have lower critical shear stresses than that of PE, which crystallizes in trans zigzag conformation. If we only consider relative critical shear stress for orientation development, P4MP1 is also expected to have a low critical shear stress owing to its loose helical structure and possess higher orientation than other polyolefins under the same level of stress. Diffraction patterns of P4MP1, however, show low level of orientation in all the regions of molded parts. This could result from the low shear viscosity and short relaxation time of P4MP1. In order to evaluate relative development of crystalline orientation among different polymers, more objective criteria are still necessary to be set. In next chapter, efforts were made to study orientation development of molded parts processed under constant injection pressure for equivalent flow stress during mold filling.

5.3.6 Crystallinity Variations among Injection Molded Polyolefins

General tendency of crystallinity variation as a function of depth in the injection molded polyolefin parts showed monotonic increase from the mold surface to the core, with the crystallinities ranging from 60 % to 67 % for PE, 56 % to 63 % for PP, 54 % to 58 % for PB1N, and 48 % to 55 % for P4MP1.

This general increase of crystallinity from the mold surface to the core has been attributed to the longer cooling times given to the deeper portion of the mold to crystallize, while quenching near the surface has been understood not to allow the material sufficient time for crystallization [159,161]. In the region close to the mold wall,
however, there seemed a certain variation of crystallinity having a resemblance with birefringence profiles in our experiments, which might be attributed to the effects of flow induced crystallization.

5.3.7 Effect of Processing Parameters on Orientation Development

Studies of the relation between orientation development and the effects of processing conditions of injection molded polyolefins have been performed by numerous researchers, and include atactic polystyrene (PS) [138-146], high density polyethylene (PE) [154-160], isotactic forms of polypropylene (PP) [162-166], polybutene-1 (PB1) [173,174] and poly(4-methyl pentene-1) (P4MP1) [177-179]. We have discussed and compared with these literature.

We found in our studies that increases of injection rate had little effect on birefringence in the core zone, but that the increased rate increases the magnitude of birefringence in the skin and transition layers and decreases their thicknesses. This can be interpreted as follows. The level of molecular orientation during the mold filling stage results from competition between flow stress and cooling history on the molten melt, and shearing history during mold filling is determined by the magnitude and length of shearing action. The closer the melt to the mold wall, the higher the shear stress. As injection rate increases, the magnitude of shearing action increases and results in increase of molecular orientation. Shearing time, however, decreases with increase of injection rate and allows less time for the melt to cool down effectively during the filling stage. All of these result in the development of higher shear rates at the locations closer to the mold wall.
During the packing stage of injection molding, additional melt flows into the mold and compensate for the volumetric shrinkage in the process of cooling. Increase of packing pressure from 10 MPa to 70 MPa resulted in increase of orientation in the core region only. This would seem because only the molecular chains in the unsolidified regions are affected by imposition of the additional melt.

Variation in mold temperature as well as in inlet melt temperature directly affects the cooling of polymer melt and therefore has a great influence in determining the level and distribution of birefringence along the thickness direction in the mold. It was observed that the skin and transition layer thicknesses decrease and birefringence maxima shifted closer to the mold wall with the increase of mold temperatures from 43 °C to 61 °C for PE (Thermal condition A to B in Figure 5.2) and from 43 °C to 154 °C (Thermal condition A to B in Figure 5.5) for P4MP1, which showed little birefringence owing to its very low intrinsic birefringence, but still exhibited the effect of mold temperature variation in its birefringence profile. With higher mold temperature, polymer melts experience a milder cooling process, which results in a shift of shear rate distribution closer to the mold wall. Consequently, the shear-induced crystallization develops closer to the mold wall, giving rise to decreases in thicknesses of the skin and transition layers. To the contrary, polymer melt experiences an increased cooling effect from larger undercooling, which results in increase of skin layer thickness, as the mold temperature decreases. Higher shear rates, therefore, develop further away from the mold wall and birefringence penetrates deeper along the thickness direction of the mold.
The effect of inlet melt temperature on birefringence can be interpreted from injection molded PB1 shown in Figure 5.4. With the decrease of inlet melt temperature from 200 °C (thermal condition A) to 180 °C (thermal condition B), higher birefringence peaks move further away from the mold wall. As the inlet melt temperature decreases, the higher viscosity of the inlet melt would result in higher level of stress under the same injection rate and the relaxation time would increase with Arrhenius type temperature dependence, which results in the development of the thicker skin layer.

5.4 Conclusions

We investigated the orientation and crystallization development of injection molded polyolefins with constant volumetric injection rate in this chapter.

The effect of processing parameters such as injection rate, packing pressure, mold temperature and inlet melt temperatures on orientation were sought to be explained through birefringence and WAXD diffraction patterns for qualitative crystalline orientation. As injection rate increases, skin and transition layers move closer to the mold wall with higher level of molecular orientation while increase of packing pressure only enhances the orientation in the core zone. Increase of mold temperature decreases cooling effect and brings skin and transition layers closer to the mold wall. Increase of inlet melt temperature decreases relaxation time of polymer melt and results in thinner skin and transition layers with lower level of orientation.

Crystal structures of injection molded polyolefin parts were investigated through WAXD 2θ scanning and it was found that only isotactic polypropylene exhibits
polymorphism consisting of \( \alpha \)-monoclinic and \( \beta \)-hexagonal crystal. The relative amount of \( \beta \)-hexagonal crystal was found to vary through the thickness direction of the mold and increase with shear stress.

The degree of crystallinity of polyolefins also varied along the mold depth. In the region close to the mold wall, the trend of crystallinity variation had a resemblance with birefringence profile, which might be attributed to the effect of flow induced crystallization. After this region, crystallinity increases monotonically to the middle of the molded part owing to increased crystallization from milder cooling environment.
CHAPTER VI
STRUCTURE DEVELOPMENT IN CONSTANT PRESSURE INJECTION MOLDING

6.1 Introduction

The main purpose of this chapter is to determine and develop an understanding of structural variations in injection molding of various polyolefins in a quantitative manner. Qualitative studies were described in the previous chapter for injection molded polyolefin parts using constant injection rates. These mainly revealed the effects of processing parameters on the development of total and crystalline orientation. However, it lacked systematic comparison among different polyolefins under an objective perspective since different material properties result in different thermal and/or mechanical history which various polymer melts would experience during mold filling.

As observed in earlier melt spinning studies [194,195,224], the development of microstructure such as molecular orientation and morphology in melt processed crystalline thermoplastics is better correlated to the level of stress applied than with kinematics. For a similar study of injection molding, it is necessary to compare resulting structures of different polymers at equivalent stress levels. It seems clear that this equivalent stress can be achieved by controlling pressure in injection molding process. This follows from the equation of motion described in Eq. (2.35), i.e.,

\[-\frac{\partial p}{\partial x_1} + \frac{\partial \sigma_{12}}{\partial x_2} = 0\]  

(6.1)
the level of stress during mold filling becomes proportional to the pressure gradient ($\sigma \sim \dot{\rho}/\dot{\lambda}$).

In order to establish this comparison of the structure development of various polyolefins, injection molding was carried out under constant injection pressure, which is equivalent to constant pressure gradient. In addition to the constant injection pressure, the thermal condition for injection molding of polyolefins should be equivalent. We have taken this to be equivalent by making the difference between the inlet melt injection temperature and the melting temperature of each polyolefin should be the same as well as the difference between the melting temperature and the mold temperature (thermal condition, B as described in Table 3.2).

Constant injection pressure coupled with the thermal condition, B would presumably provide the equivalent melt flow stress before the onset of crystallization and approximately uniform thermal history to various semicrystalline polyolefins. The development of the crystalline orientation and the morphology under the presumably equivalent flow stress fields and thermal history was investigated by experimental techniques such as wide angle X-ray diffraction (WAXD) and polarized light optical microscopy (PLOM). We have sought to relate the development of these structural features with the processing conditions by considering crystallization kinetics and rheological properties of raw materials.
6.2 General Perspective of Major Principal Axes of Orientation

Our perspective of polymer chain and crystallographic axis orientation follows Muller [123] and later authors [128,129] that orientation is expressible as a second order tensor and as an ellipsoid. In order to establish better understandings for the complex chain orientation states of injection molded parts, it is necessary to resolve whether there is any difference between the directions of major principal axes of orientation and the injection flow direction. Second order tensorial quantities such as the refractive index tensor can be used to determine the major principal axes of orientation. Atomic or molecular polarizability is phenomenologically related to refractive index through the Lorentz-Lorenz equation arguments and leads to a refractive index tensor. This refractive index tensor, \( n \) is represented in Fresnel’s ellipsoid, which can be expressed as [225]

\[
\mathbf{n}^2 \cdot \mathbf{x} \cdot \mathbf{x} = 1
\]  

(6.2)

and in the directions of the major principal axes, I, II and III

\[
n_{I}^{2}x_{I}^{2} + n_{II}^{2}x_{II}^{2} + n_{III}^{2}x_{III}^{2} = 1
\]  

(6.3)

While the refractive index ellipsoid represents integral properties from both amorphous and crystalline phases, WAXD pole figures represent a spatial distribution of plane normals of a certain crystallographic plane. Analogous to the anisotropy of polarizability and refractive index, a second order tensorial quantity, \( X \) from the WAXD pole figure data can be defined. It may be expressed as

\[
X \cdot \mathbf{x} \cdot \mathbf{x} = \sum_{i} \sum_{j} X_{ij} x_{i} x_{j} = 1
\]  

(6.4)

and in the directions of the major principal axes, I, II and III
\[ X_{11}x_1^2 + X_{22}x_2^2 + X_{33}x_3^2 = 1 \]  \hfill (6.5)

with

\[ X_{ij} = \cos \phi_i \cos \phi_j \frac{\iint I_{ijkl}(\phi, \beta) \sin \phi \cos \phi_i \cos \phi_j \, d\phi \, d\beta}{\iint I_{ijkl}(\phi, \beta) \sin \phi \, d\phi \, d\beta} \]  \hfill (6.6)

where \( \phi_i \) and \( \phi_j \) represent the polar angles of the reciprocal (hkl) plane direction with respect to the laboratory direction \( i \) and \( j \) in the pole figure, respectively. \( I \), \( II \), and \( III \) are principal axes of orientation.

Figure 6.1 Schematic representation of orientation ellipsoid

The orientation ellipsoid, which can be constructed from either refractive index or wide angle X-ray diffraction (WAXD) pole figure experiments, is schematically shown in Figure 6.1. The distance from the origin to the surface of the ellipsoid is expressed as ‘\( r \)’, which represents the experimentally determined ‘\( n^{-1} \)’ or ‘\( X^{-0.5} \)’ from refractive index or WAXD pole figure data, respectively.
In our experiments, the layers to be investigated were obtained from the middle of the molded parts, i.e. from a centrally located section between the gate and the end of the mold as shown in Figure 3.1. Therefore, because of symmetry one of three principal axes of the refractive index and orientation tensors \((III)\) should coincide with the width (3) direction and the other two major axes \((I\) and \(II)\) should be located in the plane of the flow \((1)\) – thickness \((2)\) directions. It follows that the construction of the 2-dimensional orientation ellipse schematically shown in Figure 6.2, rather than a total ellipsoid in Figure 6.1 should be sufficient to describe possible discrepancies between the machine directions and the major principal axes.

Figure 6.2 Schematic representation of 2-dimensional orientation ellipse in the flow (1) – thickness (2) plane
6.3 Results

In this section, we are going to describe the results of our measurements of the birefringence distribution, the levels of crystalline orientation and microstructures of atactic polystyrene (PS) and the various polyolefins, which were injection molded using a constant injection pressure. First, the birefringence distributions along the major principal axes at the different depths of the cross-sections were determined. This involves measuring the extinction angles. These were compared with the birefringence profiles along the machine directions. The birefringence distributions in the plane of the flow (1)-width (3) directions were also measured in order to describe the orientation characteristics in space.

Micromorphology observations have been made on these cross-sections using polarized light optical microscopy (PLOM). We have determined the levels of crystalline orientation through WAXD pole figures. Orientation ellipses of each crystallographic plane from WAXD pole figure data were also calculated and compared with the results from PLOM.

6.3.1 Birefringence

Knowledge of the angular deviation of the major principal axes from the machine directions makes it possible to evaluate the birefringence distributions along the symmetry, principal axes. In order to investigate the symmetry axes distribution in the flow (1)-thickness (2) plane of injection molded parts, the layers were cut along the center line as shown in Figure 3.1 such that one of three principal axes (III) should coincide with the transverse, width direction (3) from the geometric symmetry. When the
principal axes I and II coincide with the flow and thickness directions, respectively, the fringe patterns of the layer with respect to the center line would become symmetric at any rotation under crossed polarizers with a Berek compensator. For the case, however, where the principal axes are not in accordance with the flow and thickness directions and instead make a extinction angle with them, asymmetric fringe patterns with respect to the center line would be found as the layer rotates except at the position of 45° between two crossed polarizers.

The isoclinic or extinction angle, \( \chi_{II} \) defined as the angle between the flow (I) direction and the principal axis, I was determined by measuring the angular position of extinction occurrence of a specific region as a function of depth in the microtomed layers. By centering a specific position in the thickness direction of the layer and rotating the sample mounting stage from the initial location where the flow direction of the layer corresponds to one of two optical axes of perpendicularly crossed polarizers, we found the extinction angle for that specific position and determined \( \chi_{II} \). Then, this extinction angle can be incorporated into the relation between birefringences in the frames of principal axes and machine directions in a simple shear flow as

\[
\Delta n_{I,II} = \frac{\Delta n_{II}}{\cos 2\chi_{II}} \quad (6.7)
\]

6.3.1.1 Atactic Polystyrene

In the previous chapter, birefringence profile of polystyrene (PS) were presented based on differences of refractive indices along the flow and thickness directions. This had the implicit assumption that the flow and thickness directions represent the symmetry
Figure 6.3 Extinction angle distribution of principal axis along thickness in the 1-2 plane of injection molded PS

Figure 6.4 Distributions of experimentally determined principal birefringence \((n_I-n_{II})\) and pseudo-birefringence \((n_{11}-n_{22})\) in the 1-2 plane of injection molded PS
of the orientation directions in the molding. In general, however, the symmetry axes of orientation are not known and they can differ from the flow and thickness directions in injection molded parts due to complex thermal and mechanical stresses [158,165].

The distribution of the extinction angle, $\chi_{II}$ is shown in Figure 6.3, which indicates the variations of the extinction angles in the principal axes of the refractive index ellipses in the 1-2 plane. The extinction angle of the principal axes ranges from $0^\circ$ to $27^\circ$. There is no distinguishable extinction angle in the core region, while there are significant variations of the extinction angle in the region close to the mold wall.

The principal birefringence distributions ($n_1 - n_{III}$) corresponding to the extinction angle in the 1-2 plane of the center line are shown in Figure 6.4. Compared with the distribution of pseudo-birefringence ($n_{11} - n_{22}$) determined along the coordinates of the molded part, the principal birefringence exhibits up to 60% higher values in the region close to the mold wall but the same low values as the pseudo-birefringence in the core region.

6.3.1.2 Polyethylene

In the case of the polyolefins, we sought to measure ($n_{11} - n_{33}$) as well as ($n_{11} - n_{22}$) to completely characterize the refractive index ellipsoid. Figure 6.5 shows the variations of the extinction angles in the 1-2 plane as a function of thickness in the PE parts injection molded using two different thermal conditions under the constant injection pressure of 65.5 MPa (Thermal condition, A: $T_{\text{melt}} = 200 ^\circ \text{C}$ & $T_{\text{mold}} = 43 ^\circ \text{C}$ & Thermal condition, B: $T_{\text{melt}} = 198 ^\circ \text{C}$ & $T_{\text{mold}} = 61 ^\circ \text{C}$). The maximum $\chi_{II}$ angle only reaches $5^\circ$ in the intermediate region close to the mold wall and there is little difference between its
Figure 6.5 Extinction angle distribution of principal axis along thickness in the 1-2 plane of injection molded PE

Figure 6.6 Principal birefringence profile as a function of depth from the surface to the core of injection molded PE using injection pressure of 65.5 MPa
values at the two thermal conditions. In the mold wall region and wide range in the middle of the molded parts, no appreciable extinction angle is observed.

The principal birefringence profiles across the cross sections of molded PE are shown in Figure 6.6. Owing to the small variations of the extinction angle, there is no meaningful difference observed between \((n_{11} - n_{22})\) and \((n_1 - n_II)\). The principal birefringence profiles show a decrease from the surface to the core of the mold, ranging from \(15 \times 10^{-3}\) down to \(5 \times 10^{-3}\) for thermal condition, B while exhibiting slightly higher values for the case of thermal condition, A. The birefringence peaks also made shifts closer to the mold wall with increase of mold temperature.

![Figure 6.7 Principal birefringence profiles of injection molded PE along the major principal axes, \(\Delta n_{II,II}, \Delta n_{III,II}, \text{ and } \Delta n_{I,III}\)](image)

The measurement of the birefringence in the 1 (MD) – 3 (TD) plane was also carried out since it is not sufficient only with the birefringence distribution in the 1 (MD) – 2 (ND) plane to fully describe the characteristics of the refractive index ellipsoid. As
shown in Figure 6.7, the values of \((n_1 - n_{III})\) were much smaller compared with those of \((n_1 - n_{II})\), which resulted in very little differences between \((n_1 - n_{II})\) and \((n_{III} - n_{II})\) in both thermal conditions.

6.3.1.3 Isotactic Polypropylene

Figure 6.8 shows the variations of the extinction angles as a function of thickness in the PP parts injection molded using two different thermal conditions under the constant injection pressure of 65.5 MPa (Thermal condition, A: \(T_{\text{melt}} = 200^\circ C \& T_{\text{mold}} = 43^\circ C\) & Thermal condition, B: \(T_{\text{melt}} = 228^\circ C \& T_{\text{mold}} = 91^\circ C\)). Distinguishable variations are observed around 25 % depth with extinction angles reaching up to 8\(^\circ\). In the mold wall and the core region, there is no extinction angle observed.

From its very low level of extinction angle, PP molded parts exhibited essentially the same distributions for \((n_{11} - n_{22})\) and \((n_1 - n_{II})\). The maximum principal birefringence values of PP injection molded parts reached \(20 \times 10^{-3}\) for both cases of thermal conditions as shown in Figure 6.9. Three distinct sublayers consisting of the skin, the transition layers and the core, were clearly distinguished and the birefringence profile of the skin layer exhibited very high gradients in the thickness direction, showing quite high birefringence values of \(18 \times 10^{-3}\). After the transition layer, which was located at 10 ~ 20 % of total depth of the mold, birefringence decreased very rapidly and stayed at low values of \(3 \times 10^{-3}\) down to the core. As observed in rate-controlled injection molded samples, increases of both inlet melt and mold temperatures in thermal condition, B (\(T_{\text{melt}} = 228^\circ C \& T_{\text{mold}} = 91^\circ C\)) from the thermal condition, A (\(T_{\text{melt}} = 200^\circ C \& T_{\text{mold}} = 43\))
Figure 6.8 Extinction angle distribution of principal axis along thickness in the 1-2 plane of injection molded PP

Figure 6.9 Principal birefringence profile as a function of depth from the surface to the core of injection molded PP using injection pressure of 65.5 MPa
°C,) brought birefringence curve closer to the mold surface and showed a slightly lower value in the core region.

The values of \((n_i - n_{III})\) were essentially same as those of \((n_i - n_{II})\), which resulted in almost no birefringence, \((n_{III} - n_{II})\), in both thermal conditions of PP injection molded parts as shown in Figure 6.10.

Figure 6.10 Principal birefringence profiles of injection molded PP along the major principal axes, \(\Delta n_{I,II}, \Delta n_{III,II}, \) and \(\Delta n_{I,III}\)

6.3.1.4 Isotactic Polybutene-1

Figure 6.11 shows the extinction angle distributions across the cross-sections of molded PB1 and PB1N with two different thermal conditions (thermal condition, A: for both, \(T_{melt} = 200 \, ^\circ C \) & \(T_{mold} = 43 \, ^\circ C\), thermal condition, B for PB1: \(T_{melt} = 177 \, ^\circ C \) & \(T_{mold} = 40 \, ^\circ C\) and for PB1N: \(T_{melt} = 180 \, ^\circ C \) & \(T_{mold} = 43 \, ^\circ C\)) at the injection pressure of 65.5 MPa. The extinction angle variations for non-nucleated PB1 and nucleated polybutene-1 PB1N are similar and the maximum extinction angle from PB1 (13\(^\circ\)) is slightly higher
than that from PB1N (8°). They show very small extinction angle in the mold wall and the core region and the higher extinction angles are in the intermediate region.

Principal birefringence values calculated from corresponding extinction angles exhibited no observable difference from \((n_{11} - n_{22})\). The principal birefringence distributions across the cross-sections of molded PB1 and PB1N are shown in Figure 6.12. In PB1, it seems that decrease in inlet melt temperature shifted birefringence peaks deeper in the thickness direction. While first maximum of birefringence from both conditions exhibited values of \(12 \times 10^{-3}\) in the region very close to the mold wall (~2.5% of total depth), the second maxima appeared at 6.5% depth with \(10 \times 10^{-3}\) for the case of thermal condition, A and at 10% depth with \(9 \times 10^{-3}\) for the case of thermal condition, B, respectively. Passing through these second maxima, the birefringence decreased to \(1 \times 10^{-3}\) in the core region.

In case of PB1N, similar behavior was observed as those of non-nucleated polybutene-1, PB1. Figure 6.12 b) shows almost same birefringence profiles as those in Figure 6.12 a), except that the birefringence profiles show more distinguishable second maxima in PB1N than those in PB1.

In both PB1 and PB1N cases, the values of \((n_l - n_{ll})\) were almost same as those of \((n_l - n_{ll})\), which resulted in little birefringence, \((n_{ll} - n_{ll})\) as shown in Figure 6.13 and Figure 6.14, respectively.
Figure 6.11 Extinction angle distributions of principal axis along thickness in the 1-2 plane of injection molded a) PB1 and b) PB1N

Figure 6.12 Principal birefringence profiles as a function of depth from the surface to the core of injection molded a) PB1 and b) PB1N using injection pressure of 65.5 MPa
Figure 6.13 Principal birefringence profiles of injection molded PB1 along the major principal axes, $\Delta n_{\text{I,II}}$, $\Delta n_{\text{III,II}}$, and $\Delta n_{\text{I,III}}$

Figure 6.14 Principal birefringence profiles of injection molded PB1N along the major principal axes, $\Delta n_{\text{I,II}}$, $\Delta n_{\text{III,II}}$, and $\Delta n_{\text{I,III}}$
6.3.1.5 Isotactic Poly(4-methyl pentene-1)

Figure 6.15 Birefringence profile as a function of depth from the surface to the core of injection molded P4MP1 using injection pressure of 65.5 MPa

The investigation of extinction angle distributions in injection molded P4MP1 is discouraged by its very low intrinsic birefringence at room temperature. We were not able to obtain reliable data. Figure 6.15 shows the birefringence \((n_{11} - n_{22})\) profiles of P4MP1 injection molded at 65.5 MPa with two different thermal conditions (A: \(T_{\text{melt}} = 291^\circ\text{C} \& T_{\text{mold}} = 43^\circ\text{C}\), B: \(T_{\text{melt}} = 291^\circ\text{C} \& T_{\text{mold}} = 154^\circ\text{C}\)). A skin-core morphology was not observed and instead very low birefringences are prevalent along the whole depth of the sample. In both thermal conditions, P4MP1 shows no appreciable birefringence in the region close to the mold wall and very low birefringence, of which maximum is less than \(0.8 \times 10^{-3}\) throughout the mold.
6.3.2 Crystalline Morphology by Polarized Optical Light Micrographs

Crystalline morphologies for various injection molded polyolefins were investigated using polarized optical light photomicrographs. Variations in features and ranges of morphological layers were presented according to different depth as well as different thermal conditions, A and B, for thin microtomed layers (~ 20 µm) in the 1(MD) – 2 (ND) plane from molded parts processed at the injection pressure of 65.5 MPa. Layers to be investigated were prepared as described in Section 3.5.1 and each photomicrograph was indexed with the type of thermal condition and the angle between the axes of two perpendicularly crossed polarizers and the injection flow direction of the layer.

6.3.2.1 Polyethylene

Crystalline morphologies in injection molded PE are shown in Figure 6.16. The general tendency of morphology observed along the thickness direction is as follows for both thermal conditions, A (T_{melt} = 200 °C & T_{mold} = 43 °C) and B (T_{melt} = 198 °C & T_{mold} = 61 °C). A birefringent structure oriented along the machine direction (MD) was observed in the skin layer. This contained bright lines arranged in rows, running parallel to the surface of the molding. A transition layer is found below the skin layer which exhibits small asymmetric spherulites (~ 5 µm) and oblate spherulites of rather larger size (~ 15 µm). In the core region, we find typical spherulites of dimensions of ~ 25 µm. It is also found that the skin and the transition layers move closer to the mold wall with increase of the mold temperature from the thermal condition A to B.
6.3.2.2 Isotactic Polypropylene

The morphology of injection molded PP was determined under different thermal conditions, condition A (T\text{melt} = 200 °C & T\text{mold} = 43 °C) and condition B (T\text{melt} = 228 °C & T\text{mold} = 91 °C), and they are shown in Figure 6.17. The increases of the inlet melt and mold temperatures for condition B result in much thinner skin and transition layers (~150 µm) than in thermal condition, A (~400 µm). Larger spherulites (~45 µm) are observed in the core region of molded PP parts under condition B than those under condition A (~35 µm). The general morphological features show that the non-spherulitic structure of the skin layer exhibits a fine oriented grain structure and the next transition
layer, between the skin layer and the core region of well-defined spherulitic structure, exhibits structures of fine spherulites.

![Figure 6.17 Polarized optical light micrographs of PP injection molded at 65.5 MPa with scale bar in the middle (smallest scale: 100 µm)](image)

### 6.3.2.3 Isotactic Polybutene-1

Three distinct regions of the injection molded non-nucleated polybutene-1, PB1 are shown in Figure 6.18. These include a skin layer, the transition layer, and a core zone. The skin layer consist of almost dull or featureless outer band and inner band of many compact tiny bright lines almost perpendicular to the mold surface when viewed at 0° or 90° between the injection flow direction and the axes of two crossed polarizers. The transition layer below the skin layer exhibits oblate spherulites with their short axes
parallel to the injection direction, which is followed by a spherulitic core. The spherulites have dimensions of \( \sim 50 \, \mu m \).

Figure 6.18 Polarized optical light micrographs of PB1 injection molded at 65.5 MPa with scale bar in the middle (smallest scale: 100 \( \mu m \))

Slight decreases in both inlet melt and mold temperatures in thermal condition, B \( (T_{melt} = 177 \, ^\circ C \, \& \, T_{mold} = 40 \, ^\circ C) \) doesn’t seem to produce noticeable variations compared with the case of thermal condition, A \( (T_{melt} = 200 \, ^\circ C \, \& \, T_{mold} = 43 \, ^\circ C) \). Similar morphological features are found in nucleated polybutene-1, PB1N in Figure 6.19. The spherulites in the core region, however, keep their oblate characteristics in both thermal conditions, which have dimensions of \( \sim 35 \, \mu m \).
Figure 6.19 Polarized optical light micrographs of PB1N injection molded at 65.5 MPa with scale bar in the middle (smallest scale: 100 µm)

6.3.2.4 Isotactic Poly(4-methyl pentene-1)

Figure 6.20 shows polarized optical micrographs of injection molded P4MP1 layers. These show no distinguishable crystalline morphology except in the region close to the mold surface. When the layers were placed at the angle of 45°, bright image consisting of fine grains are observed in the skin layer from thermal condition, A ($T_{\text{melt}} = 291 ^\circ \text{C}$ & $T_{\text{mold}} = 43 ^\circ \text{C}$). When the mold temperature increases in thermal condition, B ($T_{\text{melt}} = 291 ^\circ \text{C}$ & $T_{\text{mold}} = 154 ^\circ \text{C}$), well-defined stacks of bright lines, which are perpendicular to the mold surface, are observed right below a non-spherulitic skin structure.
6.3.3 WAXD Pole Figures

Quantitative crystalline orientation levels of various semicrystalline polyolefins were investigated through WAXD pole figure measurements. Layers of different regions as a function of distance from the surface to the core were investigated for the injection molded polyolefin parts, which were molded at 65.5 MPa and thermal condition, B as described in Section 3.4. Appropriate coordinate transformations were made to create meridional stereographic nets (TD(transverse direction)-centered). We sought to investigate the orientation texture of various crystalline planes of polyolefins as well as
calculate the deviations of principal or symmetry axes from the machine directions and compare their variations as a function of thickness.

6.3.3.1 Polyethylene

Two crystallographic planes were selected for investigating crystalline orientation of high density polyethylene (PE), which are (110) and (200) at 21.7° and 24.1° for the Bragg 2θ angle. The (110) plane represents a combination of the a- and b-axes and the pole figures from the (200) plane represent the orientation of a-axis.

WAXD pole figures for the layers of injection molded PE are shown in Figure 6.21 and their relative positions along the thickness direction are indicated with the normalized distance from the surface, z/H. MD represents the machine, flow direction, ND the normal, thickness direction, and TD the transverse, width direction, respectively. The (110) and (200) plane normals in the region close to the mold wall show that the b-axis is oriented along ND, while a- and c-axes are distributed in the plane of MD and TD. As we approach deeper to the core region, the orientation becomes randomly distributed.
Figure 6.21 WAXD Pole figures of PE injection molded at 65.5 MPa and thermal condition, B \((T_{\text{melt}} = 198^\circ \text{C} \& T_{\text{mold}} = 61^\circ \text{C})\)

6.3.3.2 Isotactic Polypropylene

Figure 6.22 shows the pole figure patterns of the (040) and (110) crystalline planes for the injection molded isotactic polypropylene (PP) parts, of which reflections were found at 14.2° and 17.1° of the corresponding 2θ angle. The b-axis orientation behavior can be interpreted from the (040) reflection, while the combination of the a*- and b-axes
Figure 6.22 WAXD Pole figures of PP injection molded at 65.5 MPa and thermal condition, B \( (T_{\text{melt}} = 228 \, ^{\circ}\text{C} \text{ & } T_{\text{mold}} = 91 \, ^{\circ}\text{C}) \)

orientation is represented in the (110) reflection, where we define the axis perpendicular to the b- and c-axes as the a*-axis. PP exhibits orientation texture of high order, especially in the region close to the mold wall, which is largely uniaxial. In this region, the c-axis is oriented close to the flow direction, MD and the b-axis lies in the plane perpendicular to the MD. The level of orientation decreases rapidly in approaching the
middle of the molded part and eventually becomes randomly oriented in the core region. The pole figure patterns in the first layers \((z/H = 0 \sim 0.03125)\) of each plane show that the largely uniaxial patterns do not lie on the equator perfectly, instead making some angles to it. This seems to be because the direction of the major principal orientation axes may not be in the machine directions.

6.3.3.3 Isotactic Polybutene-1

![Image](image.png)

Figure 6.23 WAXD Pole figures of PB1 injection molded at 65.5 MPa and thermal condition, B \((T_{\text{melt}} = 177 \, ^{\circ}C \, \& \, T_{\text{mold}} = 40 \, ^{\circ}C)\)

The crystalline orientation behavior of isotactic polybutene-1 (PB1) can only be described through a single crystalline plane reflection from the geometric nature of its hexagonal unit cell. We investigated the WAXD reflection of the \((300)\) plane, of which 20 angle is located at 17.4°.

Figure 6.23 shows the orientation texture of PB1. As observed in the case of PP, PB1 exhibits uniaxial orientation mostly in the surface region of the mold, where the a- or
b-axis is distributed in the plane normal to the flow direction with the c-axis orientation along the flow direction. More random orientation is observed with deeper positions in the thickness.

In Figure 6.24, nucleated polybutene-1 (PB1N) exhibits fairly similar orientation textures with those of non-nucleated polybutene-1, PB1. The effect of nucleation seems to allow the crystalline orientation to penetrate deeper with PB1N.

Figure 6.24 WAXD Pole figures of PB1N injection molded at 65.5 MPa and thermal condition, B ($T_{melt} = 180^\circ C \& T_{mold} = 43^\circ C$)

6.3.3.4 Isotactic Poly(4-methyl pentene-1)

WAXD pole figures from the (200) crystalline plane of the tetragonal unit cell of isotactic poly(4-methyl pentene-1) (P4MP1) are shown in Figure 6.25. In the first layer, which is the skin layer from the mold surface to the depth of ~3 % of total depth from the surface to the core, the pole figure represents the orientation texture somewhat like that of a single crystal. In this region, the a-, b- and c-axes are in the directions corresponding to
the transverse (TD), normal (ND) and the flow (MD) directions, respectively. Passing through the first skin layer and approaching deeper in the thickness direction, the c-axis orientation seems to change from the MD-orientation to ND-orientation. It becomes clear that starting from the depth of $z/H = 0.25$, the c-axis is oriented along ND all the way down to the core with the a- and b-axes are distributed in the plane parallel to the mold surface.

![WAXD Pole figures of P4MP1 injection molded at 65.5 MPa and thermal condition, B (T\text{melt} = 291 \degree C & T\text{mold} = 154 \degree C)](image)

Figure 6.25 WAXD Pole figures of P4MP1 injection molded at 65.5 MPa and thermal condition, B ($T_{\text{melt}} = 291 \degree C & T_{\text{mold}} = 154 \degree C$)

6.3.4 Crystalline Orientation Factors

The levels of crystalline orientation in polyolefin molded parts (Injection Pressure: 65.5 MPa and Thermal Condition: B) were determined quantitatively from the pole figure data presented in the previous section. The preferred orientation in each layer was represented in the machine direction in these pole figures. It has been argued, however, by several investigators [158,165] that the direction of the major principal axis of
orientation should not be uniquely in the flow direction but tilted to it in the complex chain orientation state of injection molded parts. The degree of extinction angle along the thickness direction of the molded polyolefins including amorphous polystyrene were investigated from the refractive index ellipse through the interpretation of fringe patterns as described in Section 6.3.1. The general state of the orientation ellipse for the injection molded semicrystalline polyolefin parts were also generated by the application of the mean cosine squared ellipses, which could be constructed from the pole figure data as described in Section 6.2. The direction of the major principal axis was, then, estimated by the least square methods and the crystalline orientation factors were calculated along the directions of the principal axes. They were represented in terms of the White-Spruiell biaxial orientation factors [129] as a function of distance from the surface to the core of the mold.

6.3.4.1 Polyethylene

In birefringence measurements in PE injection molded parts, the direction of major principal axis did not coincide with the flow direction. It made, instead, a extinction angle to it. From the analysis of WAXD pole figure data, the extinction angle as a function of distance from the mold surface varies from $0^\circ$ to $8^\circ$. The behavior of extinction angle along the thickness direction of the molded PE is compared with that of PS and shown in Figure 6.26. The general tendency of extinction angle from two crystalline planes of PE, (110) and (200), shows that the variation of extinction angle is more complicated in PE than in PS, and the degree of PE extinction angle is much smaller than that of PS, especially in the surface region. The deviation of principal axis
from the flow direction becomes larger in PE than in PS in the intermediate region. In the core region, there seems to be little deviation of principal axis from the flow direction in both polymers. This general tendency of extinction angle variations from WAXD pole figure data seems to be in good agreement with that from birefringence measurements.

![Extinction angle distribution of principal axis along thickness from WAXD characterization of two crystalline planes of PE injection molded at 65.5 MPa and thermal condition, B](image)

Figure 6.26 Extinction angle distribution of principal axis along thickness from WAXD characterization of two crystalline planes of PE injection molded at 65.5 MPa and thermal condition, B

The quantitative level of biaxial crystalline orientation factors for the injection molded PE was determined from the diffraction intensities of the (110) and (200) reflections. We applied Wilchinsky’s equation [226] and orthogonal relationships of three unit cell axes (a-, b- and c-axis) as shown in Eq.(6.8).

\[
\cos^2 \phi_{ax} = 1 - 1.445 \cos^2 \phi_{110,z} - 0.555 \cos^2 \phi_{200,z}
\]

\[
\cos^2 \phi_{bx} + \cos^2 \phi_{cx} = 1
\]

(6.8)
Figure 6.27 Biaxial orientation a) factors and b) triangle of PE injection molded at 65.5 MPa and thermal condition, B as a function of normalized distance from the mold surface, z/H
Figure 6.27 shows the biaxial crystalline orientation factors and triangle determined for the molded PE sample which was used for pole figure measurements in Figure 6.21. Since the level of extinction angle in the molded PE was relatively small, the maximum angle being $11^\circ$, there wasn’t a distinguishable difference between the plots of $f_B^1$ versus $f_B^2$ and the plots of $f_B^I$ versus $f_B^{II}$. As observed in the pole figure, it can be seen in Figure 6.27 a) that the b-axis is oriented perpendicular to the mold surface in the region close to the mold wall, while the a- and c-axes are more randomly distributed in the plane perpendicular to the mold surface. As we approach to the core, the biaxial orientation factors of the b-axis along the flow direction and the normal direction decreases rather rapidly with the slight increase in the biaxial orientation factors of the a- and c-axes along the flow direction.

The biaxial orientation factors on the White-Spruiell biaxial orientation triangle are shown in Figure 6.27 b). In the plane of the flow (I) – transverse (III) directions, they tend to be located on the altitude of the triangle and at the origin as approaching the middle of the molded part.

6.3.4.2 Isotactic Polypropylene

The crystalline orientation factors were determined from the WAXD intensities of the (040) and (110) reflections of the monoclinic $\alpha$ unit cell for the injection molded PP parts. The extinction angle of the major principal axis against the machine direction of those crystalline planes varied similarly with PE, ranging from $0^\circ$ to $16^\circ$.

Wilchinsky’s method [227] and orthogonal relationships of three unit cell axes ($a^*$-, b- and c-axis) were applied for the calculation of the crystalline orientation factors. The
\[
\cos^2 \phi_{c,z} = 1 - 1.099\cos^2 \phi_{10,0} - 0.901\cos^2 \phi_{110,0} \\
\cos^2 \phi_{b,c} + \cos^2 \phi_{z,0} + \cos^2 \phi_{c,z} = 1
\] 

(6.9)

a*-axis was defined to be orthogonal to both b- and c-axes in the monoclinic unit cell and represent the a-axis orientation. The biaxial crystalline orientation factors in the plane, of which normal is parallel with the transverse, width direction of the mold, are shown in Figure 6.28 Extinction angle distribution of principal axis along thickness from WAXD characterization two crystalline planes of PP injection molded at 65.5 MPa and thermal condition, B

Figure 6.29 a) and the orientation triangle in Figure 6.29 b) along the direction of the principal axis for the injection molded PP. In Figure 6.29 a), the c-axis chain orientation factor, \(f^c_{l,c}\) showed the maximum at the skin and decreased towards zero with moving closer to the core (\(z/H = 1\)). While the b-axis orientation factor, \(f^b_{l,b}\) showed the
Figure 6.29 Biaxial orientation a) factors and b) triangle of PP injection molded at 65.5 MPa and thermal condition, B as a function of normalized distance from the mold surface, z/H
minimum at the skin and increased towards zero with moving closer to the core, the a*-axis orientation factor, $f_{I,a^*}$ exhibited the characteristics of the random orientation of the a-axis along the whole thickness level.

In the biaxial orientation triangle shown in Figure 6.29 b), the b- and c-axes are along the major principal axis, which is close to the machine, flow direction. It seems that the a*-axis orientation mainly remains in the origin of the triangle.

6.3.4.3 Isotactic Polybutene-1

Isotactic polybutene-1 exhibited the hexagonal Form I crystal structure in its aged injection molded parts and we investigated the a-axis orientation from the crystalline plane, (300). The c-axis orientation, then, can be calculated from the relation as

$$\cos^2 \phi_{c,z} = 1 - 2\cos^2 \phi_{300,z}$$

(6.10)

The biaxial crystalline orientation factors of PB1 and PB1N are shown in Figure 6.30 b) and c), respectively. They were represented along the major principal axis, which showed variations from 0° to 11° of non-nucleated polybutene-1, PB1 and from 0° to 5° for nucleated polybutene-1, PB1N. The general tendency of the extinction angle of the principal axis obtained from WAXD pole figure data was similar with that from birefringence measurements in that the direction of the principal axis deviates most from the machine direction in the intermediate region and becomes approximately identical with the machine direction.

In both cases of polybutene-1, we observed fairly high c-axis uniaxial orientation in the skin region. As we approach to the middle of the molded part, the a- and c- axes orientation becomes randomly distributed as observed with the White-Spruiell biaxial
Figure 6.30 Extinction angle and biaxial orientation factors of b) PB1 and c) PB1N injection molded at 65.5 MPa and thermal condition, B
Figure 6.31 The biaxial orientation triangles of a) PB1 and b) PB1N injection molded at 65.5 MPa and thermal condition, B

orientation triangles in Figure 6.31. It seems that the orientation level of PB1N is somewhat higher and decreases slower from the skin to the core than that of PB1.

6.3.4.4 Isotactic Poly(4-methyl pentene-1)

We investigated the pole figure data of the (200) crystalline plane in the tetragonal unit cell of isotactic poly(4-methyl pentene-1) (P4MP1) injection molded parts. The orientation of the c-axis was calculated through the relation

$$\cos^2 \phi_{c,z} = 1 - 2 \cos^2 \phi_{200,z}$$

(6.11)

Then, the biaxial crystalline orientation factors for P4MP1 were calculated and shown in Figure 6.33. Along the major principal axis, of which variations ranged from 0° to 6° in Figure 6.32, the behaviors of the a- and c-axes orientation seemed to be similar to
Figure 6.32 Extinction angle distribution of principal axis along thickness from WAXD characterization of (200) crystalline plane of P4MP1 injection molded at 65.5 MPa and thermal condition, B.

Isotactic polypropylene and polybutene-1 previously in that the skin region exhibited strong c-axis orientation along the flow direction. Along the minor principal axis, II, however, P4MP1 shows some unique characteristics of $f_{II,a}$ and $f_{II,c}$ in Figure 6.33 a).

Unlike other polyolefins which showed random orientation in the core region, the c-axis of P4MP1 shows fairly strong orientation along the thickness, the normal direction to the mold wall while the orientation level of the a-axis around $-0.2$ ($f_{II,a} \sim -0.2$), indicates the random distribution of the a- and b-axes of the tetragonal unit cell of P4MP1. This unique characteristics is not only found in the skin region, but is persistent all the way down to the core of the mold. This characteristics can be graphically presented in the biaxial orientation triangle in Figure 6.33 b), where the biaxial orientation factors of the a- and c-
Figure 6.33 Biaxial orientation a) factors and b) triangle of P4MP1 injection molded at 65.5 MPa and thermal condition, B as a function of normalized distance from the mold surface, z/H
axes were found to maintain certain values along the thickness, the normal direction to the mold wall, instead of approaching the origin of the triangle.

6.4 Interpretation

In this section, we discuss the development of crystalline orientation and the corresponding morphological features for the various polyolefins. Comparison of the level of orientation as well as the state of orientation was made. We are also going to propose a phenomenological approach for establishing the relationship between the chain orientation of crystalline polymers and the orientation of the polymer melt prior to the onset of crystallization.

6.4.1 Orientation

The behavior of the principal axes of orientation for amorphous polystyrene exhibited different characteristics from those for semicrystalline polyolefins. In case of polystyrene, the $\chi_{II}$ angle showed the maximum value ($\sim 27^\circ$) around the mold surface and decreased to zero in the core region. The general tendency of semicrystalline polyolefins from either birefringence measurements or WAXD pole figure data showed good agreements with each other. It indicated that the major principal axis of orientation is nearly parallel to the flow direction in the region close to the mold wall and in the core of the mold. In intermediate region, the principal axis makes angles from $5^\circ$ to $16^\circ$ to the flow direction in our experiments, while Mencik et al. [165] reported the angle around $12^\circ$ for the injection molded polypropylene and Wu et al. [158] estimated an angle in the range of $8^\circ$ for polyethylene. This different behavior between the principal axes of the
vitrified and semicrystalline polymers must be explained in terms of chain reorientation during crystallization in injection molding process. The principal axes of orientation in the melt state of crystalline polymers may tend to reorient to the flow (MD) and thickness (ND) directions during crystallization since the temperature gradient in injection molding is mainly in the thickness direction and results in a crystal growth direction parallel to the thickness direction.

6.4.1.1 Atactic Polystyrene

In injection molding of atactic polystyrene (PS), the melt vitrifies into a glass and maintains the molten state orientation at the time of vitrification [2]. Birefringence measurements revealed well-defined skin-core morphology with some degree of extinction angle varying according to the position in the mold. A rather large value of extinction angle (~27°), when compared with those from semicrystalline polyolefins, was found in the skin area of the vitrified polystyrene. As we approach the core region, molecular chains have longer time to relax and lower level of extinction angle, therefore, is observed [228].

6.4.1.2 Polyethylene

The crystalline orientation textures from the pole figure data (Figure 6.21) and the corresponding biaxial orientation factors (Figure 6.27 a)) of the injection molded PE indicated that the strongest characteristic of orientation in the injection molded PE is associated with the tendency of strong b-axis orientation normal to the surface of the mold [154,156,158]. This normal b-axis orientation can probably be understood from the
fact that the crystal growth direction is in the thickness direction, which corresponds to the direction of b-axis of the orthorhombic PE unit cell.

The biaxial orientation factors have been plotted on the White-Spruiell orientation triangle (Figure 6.27 b)). They tend to be on the altitude of the triangle. They show the tendency of the b-axis orientation to be perpendicular to the principal axis and width directions, equibiaxial orientation of the a- and the c-axes along the machine and width directions especially in the skin region of the mold.

The characteristics of the equibiaxial orientation was also observed with the results from the birefringence distributions, where we found that the magnitudes of \((n_I - n_{II})\) and \((n_{III} - n_{II})\) were very close (Figure 6.7). This means that there exists equibiaxial orientation in the plane of the flow (I) – transverse (III) plane of the injection molded PE parts.

### 6.4.1.3 Isotactic Polypropylene

In injection molded PP parts, the orientation state is quite different from the PE parts. The biaxial crystalline orientation factors determined along the principal axis of orientation in Figure 6.29 showed that relatively high uniaxial orientation existed at the surface (~10% of total depth from the surface to the core) and low level of orientation dominated in the wide range of the core of the mold. This tendency could be found in the Hermans-Stein uniaxial orientation factors shown in Figure 6.34, where we present the crystalline orientation factors of both monoclinic \(\alpha\)- and hexagonal \(\beta\)-crystalline phases and also the average chain-axis (c-axis) orientation factor \(f_{c,ave}\)

\[
f_{c,ave} = (1 - K) \cdot f_{c,\alpha} + K \cdot f_{c,\beta}
\]  \( (6.12)\)
where $K$ is the relative contents of the $\beta$-crystalline phase. The higher level of orientation in the $\beta$-crystalline phase in the transition layer increases the average orientation of the c-axis. This shows uniaxial characteristics in the mold surface. Before reaching the random orientation state around 25% of the total depth from the surface to the core, the c- and b-axes are fairly uniaxial while the relative orientation of the a-axis shows much less variation.

Figure 6.34 The Hermans-Stein uniaxial orientation factors along the major principal axis, $I$ of PP injection molded at 65.5 MPa and thermal condition, B

Figure 6.29 b) describes the White-Spruiell orientation triangle, which represents the uniaxial characteristics of the b- and c-axis along the major principal axis in the region close to the mold wall. This uniaxial characteristic was also observed with birefringence distribution in Figure 6.10.

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6.4.1.4 Isotactic Polybutene-1

From birefringence measurements, pole figure data and corresponding orientation triangles, it could be seen that both neat and nucleated isotactic polybutene-1, PB1 and PB1N show largely uniaxial orientation in the region close to the mold wall, similar to isotactic polypropylene. In PB1, the level of c-axis orientation decreases gradually in approaching to the core, while PB1N maintains orientation to some extent in the core. These characteristics are also found in the plot of Hermans-Stein uniaxial orientation factors as shown in Figure 6.35 and Figure 6.36. The difference between the orientation behaviors of PB1 and PB1N in the middle part of the mold can be attributed to longer relaxation time of PB1N than that of PB1 and this longer relaxation time seems to allow PB1N to keep its preferred orientation even in the core.

There have been a few previous studies on injection molding of isotactic polybutene-1 [173-176]. They were mostly concerned with the relation between mechanical properties and morphology and are lacking in quantitative orientation and corresponding microstructure development. The a- and c-crystallographic axes of hexagonal unit cell of injection molded isotactic polybutene-1 exhibit uniaxial characteristics along the flow direction in the plane of the major principal axis and transverse, width direction. In the skin area, the orientation level of PB1N is slightly higher than that of PB1, which can be attributed to the increased effect of crystallization-induced orientation. As observed in the Hermans-Stein orientation factors, PB1N exhibits certain level factors, PB1N exhibits certain level of c-axis orientation in the middle part of the mold while PB1 shows general random orientation.
Figure 6.35 The Hermans-Stein uniaxial orientation factors along the major principal axis, $l$ of PB1 injection molded at 65.5 MPa and thermal condition, B

Figure 6.36 The Hermans-Stein uniaxial orientation factors along the major principal axis, $l$ of PB1N injection molded at 65.5 MPa and thermal condition, B
6.4.1.5 Isotactic Poly(4-methyl pentene-1)

Determination of biaxial crystalline orientation factors of P4MP1 through pole figure measurements was very helpful to understand the orientation characteristics of injection molded P4MP1 since orientation studies using birefringence was largely impossible because of the low intrinsic birefringence value of P4MP1. The spatial distribution of (200) crystalline plane of tetragonal P4MP1 unit cell showed unique characteristics in the region close to the mold surface (z/H = 0~0.03125), which is somewhat similar with orientation of a single crystal. The c-axis is oriented along the flow direction, the b-axis along the normal direction, and the a-axis is oriented along the transverse direction at the skin in the first layer investigated.

Then, the orientation characteristics of the a- and the c-axis change rapidly towards the core. As shown in Figure 6.33, the c-axis tends to be oriented along the thickness, normal direction with the a-axis distributed in the flow (1)-width (3) plane. This peculiar normal orientation of P4MP1 was previously reported by Bevis et al. [178,179], who observed it under the highest inlet melt temperature (340 °C) in their moldings. Bevis et al. [178,179] proposed that the solidification tensile stress would cause this phenomenon. It seems reasonable to argue that P4MP1 molecular chains would go through the largest volumetric shrinkage and corresponding solidification tensile stress from the highest inlet melt temperature among various polyolefins in our moldings. However, we only observed the perpendicular orientation in P4MP1 under the thermal condition, B (P4MP1B), where the mold temperature of 154 °C was used, while no such orientation was found in P4MP1 under the thermal condition, A (P4MP1A), where a much lower
mold temperature (43 °C) was applied. It seems that the approach of Bevis et al. [178,179] based on the solidification tensile stress might not be sufficient to explain this phenomenon.

It has been reported by several investigators [229-232] that P4MP1 undergoes a crystalline relaxation at $T_{\alpha_c}$, which is a crystallization relaxation temperature, ranging from 120 °C to 160 °C. At this temperature range, the $\alpha_c$ relaxation for P4MP1 can be correlated to the main-chain translational mobility within the crystalline phase. Thus, given sufficient time to stay at $T_{\alpha_c}$, P4MP1 molecular chains may tend to be rearranged along the normal direction to the mold surface, which is the direction of the thermal gradient. This would explain the results of our own experiments that there was no normal orientation in P4MP1A, which can be attributed to the relatively shorter time for the crystalline relaxation to occur, while the mold temperature of 154 °C in P4MP1B molding should have provided enough time for the relaxation to take place and result in the unique perpendicular orientation of c-axis to the mold surface.

6.4.2 Crystalline Morphology

In this subsection, crystalline morphologies of the various polyolefins are interpreted. Some aspects of this are summarized based on polarized light optical microscopy (PLOM) as shown in Table 6.1.
Table 6.1 Crystalline morphologies of various polyolefins injection molded at 65.5 MPa and thermal condition, B

<table>
<thead>
<tr>
<th></th>
<th>Skin Layer Thickness ((\mu m))</th>
<th>Transition Layer Thickness ((\mu m))</th>
<th>Core Thickness ((\mu m))</th>
<th>Spherulite Size in Core ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>100</td>
<td>100</td>
<td>1390</td>
<td>25</td>
</tr>
<tr>
<td>PP</td>
<td>80</td>
<td>70</td>
<td>1440</td>
<td>45</td>
</tr>
<tr>
<td>PB1</td>
<td>80</td>
<td>100</td>
<td>1410</td>
<td>50</td>
</tr>
<tr>
<td>PB1N</td>
<td>100</td>
<td>120</td>
<td>1370</td>
<td>35</td>
</tr>
<tr>
<td>P4MP1</td>
<td>90</td>
<td>90</td>
<td>1410</td>
<td>Not observable</td>
</tr>
</tbody>
</table>

6.4.2.1 Polyethylene

The photomicrograph of Figure 6.16 shows that the skin layer of molded PE parts is about 100 \(\mu m\) thick and the transition region is characterized as a non-spherulitic, row structure with bright lines running parallel to the mold surface.

As Keller and Machin [233] proposed a model of twisted lamellae structure for this morphology, such a structure would be interpreted as stacks of lamellae with the crystal growth direction, b-axis oriented along the thickness direction and the relative orientations of the a-axis and the c-axis depending on the level of stresses applied. In the case of high stresses, untwisted lamellar structure will develop, where the c-, a- and b-axis orient along the flow, transverse and thickness directions, respectively. The level of stress applied in our molding experiments for PE does not seem to be high enough to produce this untwisting of lamellae and instead the morphology appears to be a twisted lamellar structure.
We observed the spherulitic structure in the wide range of core region with the spherulites of dimensions of ~ 25 \( \mu \text{m} \). This average diameter of PE is rather smaller than other semicrystalline polyolefins, which might be attributed to its fast crystallization kinetics as described in Section 4.2.2.

### 6.4.2.2 Isotactic Polypropylene

Heterogeneous microstructures in injection molded PP parts are also shown in Figure 6.17. As found by previous investigations [162-166], a featureless fine grain structure is observed in the skin layer, followed by fine spherulites. Texture showing preferred orientation from row-nucleated spherulites is found next, which is followed at greater depths by well-defined spherulitic core layer of low orientation.

In the transition layer, it can be seen in Figure 6.29 and Figure 6.34 that the a*-axis does not show any distinguishable orientation while b- and c-axes exhibit largely uniaxial characteristics. This can be understood from a bimodal orientation model from epitaxial lamellar branching near the surface of the injection molded PP parts proposed earlier by several investigators [167-170]. In this model, the parent lamellae have chain foldings with the c-axis oriented along the flow direction and the daughter lamellae, which grow epitaxially from the parent lamellae have their a*-axis parallel to the c-axis of the parent lamellae. Since the b-axes of the parent and the daughter lamellae have orientations in the same direction, a mixture of a*- and c-axis orientations is observed in the transition layer of injection molded PP parts.
6.4.2.3 Isotactic Polybutene-1

We found that the injection molded parts of isotactic polybutene-1 generally have four morphological zones through the thickness direction of the mold. Following the first, featureless skin layer, there exists an apparent row-structure with tiny bright lines perpendicular to the mold surface. Third, a transition layer consists of crowded bright spots, which is an indication of the formation of oblate spherulites whose short axes are parallel to the flow direction. In the very core of the mold, spherulitic structures of random orientation could be found.

While non-nucleated PB1 showed all these four features (Figure 6.18), we did not find a spherulitic core in the case of PB1N (Figure 6.19) and instead oblate spherulites were found down to the core of the mold, which caused non-zero c-axis orientation factor of PB1N as shown in Figure 6.36. PB1N has a longer relaxation time than PB1 as we experimentally determined in Section 3.3.4 and nucleating agent in PB1N would increase the crystallization onset temperature occurs. Therefore, PB1N chains in the melt state would have a shorter time to relax before the onset of crystallization and this causes the formation of oblate spherulites in the core region of injection molded PB1N, which is in accordance with previous investigations [163,174].

6.4.2.4 Isotactic Poly(4-methyl pentene-1)

It is feasible to make presumptions on possible morphologies from the WAXD orientation characteristics observed in our experiments and the previous investigations mainly done by Owen and Hull, and Bevis et al. [177-179]. The polarized optical light microscopy observations of P4MP1 are limited by its very low intrinsic birefringence.
In the region close to the mold wall, where we found high level of the c-axis orientation along the injection flow direction, the morphology of the skin can be understood as a row structure, which has its lamellae growing in the normal direction to the mold surface. Below this layer, the ‘c-axis perpendicular to the mold surface’ orientation, which may be interpreted as a result from oriented sheaf-like structures, follows the transition layer of biaxial orientation characteristics in the flow (1) – thickness (2) plane.

6.4.3 Comparative Crystalline Orientation among Various Polyolefins

The crystalline orientation development of various polyolefins under presumably equivalent flow stress and thermal history established from a constant injection pressure and thermal condition, B is compared in the present section.

It is noteworthy that the different polyolefins exhibit different behavior in crystalline orientation development. For the region close to the surface of polyethylene molded parts, we observed equibiaxial orientation characteristics, while largely uniaxial behaviors were found in injection molding of isotactic polypropylene and polybutene-1. Injection molding of poly(4-methyl pentene-1) showed the very unique feature of perpendicular orientation.

Figure 6.37 shows the c-axis orientations along the principal axes, I and II for the molded polyolefin parts under the constant injection pressure of 65.5 MPa and thermal condition, B, in which the difference between inlet melt and melting temperatures and the differences between the melting and mold temperatures were set constant among different polymers. In Figure 6.37 b), the aforementioned unique perpendicular
orientation of P4MP1 differentiate itself from other polyolefins, which show essentially random orientations along the principal axis, $II$. The relative levels of $f^B_{II,c}$ in Figure 6.37 a) show that in the surface region, two polybutene-1 grades (PB1 and PB1N) and P4MP1 have fairly high levels of orientation while PE shows the lowest and PP exhibits intermediate c-axis orientation. In the wide range of the core region, all parts show random orientation.

![Graph](image)

Figure 6.37 Biaxial orientation factors of various polyolefin injection molded parts on the plane of principal axes, $I$ and $II$ (Injection pressure: 65.5 MPa & thermal condition: B)

Taking into account of normal orientation of P4MP1 from Figure 6.37 b), which would occur around the crystalline relaxation temperature we mentioned in Section 6.4.1.5, we might be able to make a well-guessed conjecture that P4MP1 would have the highest level of molecular orientation along the flow direction right after the onset of
crystallization and PE has the lowest. Then, the comparative orientation level under equivalent pressure gradient right after the onset of crystallization would be in order of

\[ P4MP1 > PB1N \& PB1 > PP > PE \] (6.13)

It is notable that the order of crystalline orientation is in consistent with bulkiness of helices that those polyolefins conform (7/2 helix for P4MP1, 11/3 PB1, 3/1 PP, and linear for PE). Consistency between the level of crystalline orientation and bulkiness of chain conformations might be attributed to lower activation energy needed for molecular chains to be oriented when crystallized with bulkier chain conformation. It is of interest that this ordering of polymer chain orientation should be the same as previously found for melt spinning of polyolefins by Choi et al. [224] as shown in Figure 6.38.

![Figure 6.38](image)

Figure 6.38 Relative Hermans-Stein uniaxial orientation factors in melt spinning of various polyolefins as a function of spinline stress
6.4.4 Phenomenological Relation between Orientation in Melt and Crystalline States

Orientation development for flowing melts of flexible polymer chains in polymer processings including injection molding has been well known to be related to the stress field during mold filling through the Rheo-Optical rule [234-236]. Furthermore, the chain orientation in amorphous polymers vitrified under stress can be related to the stress field through the Rheo-Optical rule at vitrification [139,236]. For semicrystalline polymers, however, the chain orientation is not quantitatively determined by the Rheo-Optical rule because of the chain rearrangement following crystallization process. Instead, the level of resulting chain orientation in the semicrystalline polymers will primarily depend upon the level of orientation in the melt state before the onset of crystallization the development of morphology during crystallization, which is peculiar to the polymer.

In the present section, we make efforts to understand the relationship between the levels of orientation of the various polyolefins prior to and after the onset of crystallization. The former can be obtained by application of the Rheo-Optical rule from the calculated stress level and was compared with the latter, which could be determined experimentally through birefringence and WAXD pole figure measurements as mentioned in the previous sections.

6.4.4.1 Level of Orientation during Mold Filling

The orientation level at the end of mold filling, prior to vitrification, can be predicted by using the Rheo-Optical rule, in which the principal axes of the stress tensor and the refractive index tensor coincide and the principal birefringences are proportional to the differences in principal stresses as
\[ n_i - n_j = C\left(\sigma_i - \sigma_j\right) \]  
(6.14)

where \(C\) is the stress optical coefficient [234-236]. This Rheo-Optical rule has been found by numerous investigators to be valid for various polymers in the molten state and for amorphous polymers in the vitrified state [139,236]. For a shear flow, the Rheo-Optical rule implies that the first normal stress difference \((N_I = \sigma_{11} - \sigma_{22})\) and the shear stress, \(\sigma_{12}\) can be related through the angle between the direction of flow and the principal axes of the stress tensor, \(\chi_{II}\) as

\[ \Delta n_{I,II} = C\left(\sigma_{11} - \sigma_{22}\right) / \cos 2\chi_{11} = 2C\sigma_{12} / \sin 2\chi_{11} = C\left(\sigma_{11} - \sigma_{22}\right)^2 + 4\sigma_{12}^2\right)^{1/2} \]  
(6.15)

The empirical relationship between \(N_I\) and \(\sigma_{12}\) in commercial polystyrene can be expressed as [139]

\[ N_I = \sigma_{11} - \sigma_{22} = A\sigma_{12}^\alpha \]  
(6.16)

where

\[ \sigma_{12} \leq 4.435 \times 10^5 \text{ dynes/cm}^2 : N_I = 3.44 \times 10^{-4} \times \sigma_{12}^{1.685} \text{ dynes/cm}^2 \]

\[ \sigma_{12} \geq 4.435 \times 10^5 \text{ dynes/cm}^2 : N_I = 4.25 \times 10^{-7} \times \sigma_{12}^{2.20} \text{ dynes/cm}^2 \]  
(6.17)

From the birefringence measurements and corresponding extinction angle distribution of the molded PS parts in Figure 6.3 and Figure 6.4, \(\Delta n_{I,II}\) exhibits its maxima in the region close to the mold wall (\(\Delta n_{I,II}^{\text{Max}} = 3.18 \times 10^{-3}\) at the depth of 65 \(\mu\)m below the mold surface). Taking the stress optical constant, \(C\) as 4500 Brewster for \(\Delta n_{I,II}^{\text{Max}}\) above, \(N_I\) (=\(\sigma_I - \sigma_{II}\)) is determined as \(7.06 \times 10^6\) dynes/cm\(^2\).
In order to complete specification of the stress ellipsoid, we also consider the nature of the second normal stress difference along the principal axes, \( N_{II} (=\sigma_{II} - \sigma_{III}) \). It has been reported by several investigators [237,238] that the ratio of the second normal stress difference to the first normal stress difference, \( N_{II}/N_I \) varies from \(-0.15\) to \(-0.45\). We are going to choose the ratio of \(-0.15\) by Lee and White [237]. Then, \((\sigma_{III} - \sigma_{II}) = 1.06 \times 10^6\) dynes/cm\(^2\), and by taking the stress optical constant, \( C \) as 4500 Brewster, \( \Delta n_{III,II} \) is determined as \(4.77 \times 10^{-4}\).

The biaxial orientation factor, then, in the melt state of amorphous polystyrene (PS) before vitrification can be predicted through

\[
\begin{align*}
\beta_{I,A} & = \frac{\Delta n_{I,II}}{\Delta^o} = \frac{C}{\Delta^o}(\sigma_{I} - \sigma_{II}) = 0.0106 \\
\beta_{III,A} & = \frac{\Delta n_{III,II}}{\Delta^o} = \frac{C}{\Delta^o}(\sigma_{III} - \sigma_{II}) = 0.0016
\end{align*}
\]

(6.18)

where the intrinsic birefringence of PS, \( \Delta^o \) \(= -0.3 \) [239]. In the melt state, various polyolefins would presumably possess equivalent stress fields owing to the constant injection pressure we applied. Since \(C/\Delta^o\) should be a universal constant at a certain stress level, which is essentially independent of all material characteristics and varies weakly with temperatures, therefore, it can be suggested that the orientation state of polyolefins in the melt state should be same as that of amorphous polystyrene.

6.4.4.2 Transformation of Orientation in Semicrystalline Polyolefins

The state of chain orientation in Cartesian coordinates may be represented by a second-order tensor, \( O_{ij} \), of which component describes second moment of orientation distribution along \(ij\) direction as \( \overline{\cos \phi_i \cos \phi_j} \), where \( \phi_i \) and \( \phi_j \) represent the angles
between a chain axis and $i$ and $j$ principal axes. From its symmetric property in Cartesian coordinates, the second moment tensor, $O_{ij}$ for the most general case can be written as

$$
O_{ij} = \begin{bmatrix}
O_{11} & O_{12} & O_{13} \\
O_{12} & O_{22} & O_{23} \\
O_{13} & O_{23} & O_{33}
\end{bmatrix}
$$

(6.19)

where $O_{11} + O_{22} + O_{33} = 1$ from the Pythagorean theorem.

For uniaxial orientation, it becomes

$$
O_{ij} = \begin{bmatrix}
O_{11} & 0 & 0 \\
0 & O_{22} & 0 \\
0 & 0 & O_{33}
\end{bmatrix}
$$

(6.20)

where $O_{22} = O_{33} = \frac{1}{2} (1 - O_{11})$ and the Hermans uniaxial orientation factor can be described as

$$
f^H = \cos^2 \phi_1 - \cos^2 \phi_2 = \cos^2 \phi_1 - \cos^2 \phi_3 = O_{11} - O_{22} = O_{11} - O_{33} = \frac{1}{2} (3O_{11} - 1)$$

(6.21)

For biaxial orientation, it becomes

$$
O_{ij} = \begin{bmatrix}
O_{11} & 0 & 0 \\
0 & O_{22} & 0 \\
0 & 0 & O_{33}
\end{bmatrix}
$$

(6.22)

where $O_{11} + O_{22} + O_{33} = 1$ and the biaxial orientation factors in the 1-3 plane may be expressed as

$$
f_1^B = \cos^2 \phi_1 - \cos^2 \phi_2 = O_{11} - O_{22} = 2O_{11} + O_{33} - 1$$

(6.23)

$$
f_3^B = \cos^2 \phi_3 - \cos^2 \phi_2 = O_{33} - O_{22} = O_{11} + 2O_{33} - 1$$

(6.24)

A fourth-order orientation transformation tensor, $S_{ijkl}$, is introduced so as to phenomenologically relate two second-order orientation tensors, $O_{ij}^C$ and $O_{ij}^A$, which
describe the state of orientation after and prior to the onset of crystallization, respectively. By presuming the orientation state of crystalline phase primarily depends on that of polymer chains in the melt state and also there would not be any changes in the directions of principal axes during crystallization process, then it may be hypothesized that the fourth-order transformation tensor relating two second-order orientation tensors can be described as

\[ O_{ij}^C = S_{ijkl} O_{kl}^A \]  

(6.25)

where components of \( O_{ij}^C \) are obtained experimentally by means of WAXD pole figure measurements. The tensorial properties of \( O_{kl}^A \) for the given stress fields are determined by using the Rheo-optical rule, stating the principal axes of refractive index tensor are same as those of the stress tensor, which implies that orientation symmetry axes are also same as the principal axes of the stress tensor.

The fourth-order tensor, \( S_{ijkl} \) has 81 components, which are not all independent. From the inherent nature of symmetry in \( O_{ij} \) (\( O_{ij} = O_{ji} \)), \( S_{ijkl} \) reduces to 36 independent components. This suggests that the second-order tensor, \( O_{ij} \) can be represented in a vectorial form with 6 components and at the same time, the fourth-order tensor with 81 components reduces to second-order tensor, \( S_{ij} \) as

\[ O_{ij}^C = S_{ij} O_{ij}^A \]  

(6.26)

where \( i \) and \( j \) run from I to VI with \( O_{11} = O_I, O_{22} = O_{II}, O_{33} = O_{III}, O_{12} = O_{IV}, O_{13} = O_{V}, \) and \( O_{23} = O_{VI} \).

If we apply Eq. (6.26) to the case of uniaxial orientation, then, even simpler relationships can be obtained along the principal axes, I, II and III as
with \( S_{22} = S_{33} = S_{23}, S_{12} = S_{13}, \) and \( S_{21} = S_{31} \) for the uniaxial orientation state. Combined with the Rheo-Optical rule, the uniaxial orientation factor along the principal axes in the molten state prior to the onset of crystallization are expressed as

\[
f_A^H = \frac{1}{2} \left( 3O_i^C - 1 \right) = \frac{C}{\Delta^o} (\sigma_i - \sigma_{ii}) = \frac{C}{\Delta^o} \sigma_i
\]

and after the crystallization as

\[
f_A^H = \frac{1}{2} \left( 3O_i^C - 1 \right)

= \frac{3}{2} \left( (S_{11} - S_{12})O_i^A + S_{12} \right) - \frac{1}{2}

= (S_{11} - S_{12}) \frac{C}{\Delta^o} \sigma_i + \frac{1}{2} (S_{11} + 2S_{12} - 1)

= \frac{1}{2} \left( 3S_{11} - 1 \right) f_A^H
\]

with the assumption of random crystalline orientation at zero stress, \( f_A^H = 0 \) when \( \sigma_i = 0 \).

A similar approach can be made for the case of biaxial orientation as

\[
\begin{bmatrix}
O_i^C \\
1/2(1-O_i^C) \\
1/2(1-O_i^C)
\end{bmatrix}
= \begin{bmatrix}
S_{11} & S_{12} & S_{13} \\
S_{21} & S_{22} & S_{23} \\
S_{31} & S_{32} & S_{33}
\end{bmatrix}
\begin{bmatrix}
O_i^A \\
1/2(1-O_i^A) \\
1/2(1-O_i^A)
\end{bmatrix}
\]

where \( O_i^C = 1 - O_i^C - O_{iii}^C \) and \( O_i^A = 1 - O_i^A - O_{iii}^A \). Then, the biaxial orientation factors in the plane of the principal axes, I and III, in the molten state prior to the onset of crystallization are expressed as
\[ f_{I,A}^B = 2O_I^4 + O_{III}^4 - 1 = \frac{C}{\Delta^o} (\sigma_I - \sigma_H) \]  
(6.31)

\[ f_{III,A}^B = O_I^4 + 2O_{III}^4 - 1 = \frac{C}{\Delta^o} (\sigma_{III} - \sigma_H) \]  
(6.32)

and after the crystallization as

\[ f_{I,C}^B = 2O_I^C + O_{III}^C - 1 = (2S_{11} + S_{31} - 2S_{12} - S_{32})O_I^4 + (2S_{13} + S_{33} - 2S_{12} - S_{32})O_{III}^4 + (2S_{12} + S_{32} - 1) \]

\[ = \frac{C}{\Delta^o} \left( (2S_{11} + S_{31} - 1)(\sigma_I - \sigma_H) + (2S_{13} + S_{33} - 1)(\sigma_{III} - \sigma_H) \right) \]

\[ = (2S_{11} + S_{31} - 1) f_{I,A}^B + (2S_{13} + S_{33} - 1) f_{III,A}^B \]  
(6.33)

\[ f_{III,C}^B = O_I^C + 2O_{III}^C - 1 = (S_{11} + 2S_{31} - S_{12} - 2S_{32})O_I^4 + (S_{13} + 2S_{33} - S_{12} - 2S_{32})O_{III}^4 + (S_{12} + 2S_{32} - 1) \]

\[ = \frac{C}{\Delta^o} \left( (S_{11} + 2S_{31} - 1)(\sigma_I - \sigma_H) + (S_{13} + 2S_{33} - 1)(\sigma_{III} - \sigma_H) \right) \]

\[ = (S_{11} + 2S_{31} - 1) f_{I,A}^B + (S_{13} + 2S_{33} - 1) f_{III,A}^B \]  
(6.34)

by assuming that \( f_{I,C}^B = f_{III,C}^B = 0 \) at \( \sigma_I - \sigma_H = \sigma_{III} - \sigma_H = 0 \).

First, we are going to investigate the generalized linear relationships between two orientation tensors for the uniaxial case previously found for melt spinning of polyolefins by Choi et al. [224] as shown in Figure 6.38. The Hermans uniaxial orientation factors for the various polyolefins were determined at the spinline stress, \( \sigma_I \), ranging from 0.6 to 1 MPa, and the components of \( \Sigma_i \) for each polyolefin were derived using Eq. (6.28) and Eq. (6.29). These equations imply that there may exist a linear relationship of the crystalline orientation factor with stresses and also the possible orientation jump after the
onset of crystallization compared with the orientation level of polymer melt prior to the onset of crystallization. The average values of $S_{11}$ can be ranked as

$$P4MPI(S_{11} \approx 50) > PBI(S_{11} \approx 41) > PP(S_{11} \approx 35) > PE(S_{11} \approx 17)$$ (6.35)

and it can be said that this ranking corresponds to the tendency of orientation to increase under the equivalent stress level.

For determining the biaxial orientation factors in injection molded samples after the onset of solidification, the principal birefringence of PS was calculated through the relationship between the pseudo-birefringence and the extinction angle, and WAXD pole figure measurements were used for semicrystalline polyolefins. Comparison between the biaxial orientation factors before and after the onset of solidification are made in Table 6.2. While the vitrified PS shows no distinguishable orientation change, there exist not only significant increases of orientation, but also changes of orientation state for semicrystalline polyolefins.

The orientation transformation tensor for the molded PS parts has the characteristics of the unit tensor with $S_{11} = 1$ and $S_{13} = 0$, which can be well understood from the fact that there is no significant orientation increase in amorphous polymer. For the semicrystalline polyolefins, however, the components of the transformation tensors, $S_{11}$ and $S_{13}$, have various values, which implies that the biaxial orientation factors after the onset of crystallization are not only influenced by $(\sigma_i - \sigma_{ii})$, but also by $(\sigma_{iii} - \sigma_{ii})$. This results in the change of the crystalline orientation levels as well as the modes of the crystalline orientation state.
The tensorial components, $S_{11}$ and $S_{13}$, determined through the relationship between the biaxial orientation factors in the plane of the principal axes, $I$ (MD) and $III$ (TD), with assuming $S_{11} = S_{33}$ and $S_{13} = S_{31}$, indicate that their magnitudes increase with bulkiness of chain conformation in the crystalline region from PE to P4MP1, as observed in the case of melt spinning. In case of PB1N, $S_{11}$ shows the largest value, which seems to be caused by the effect of improved crystallization-induced orientation from the nucleating agent.

Table 6.2 Biaxial orientation factors of c-axis for various polymer melts along the principal axes, $I$ and $III$, prior to and after the onset of solidification (Depth: ~ 65 µm)

<table>
<thead>
<tr>
<th>Material</th>
<th>Prior to the Onset of Solidification</th>
<th>After the Onset of Solidification</th>
<th>Calculated Values of Tensorial Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{I,A}^B$</td>
<td>$f_{III,A}^B$</td>
<td>$f_{I,C}^B$</td>
</tr>
<tr>
<td>PS</td>
<td>0.0106</td>
<td>0.0016</td>
<td>6.7</td>
</tr>
<tr>
<td>PE</td>
<td>0.230</td>
<td>0.216</td>
<td>-24.20</td>
</tr>
<tr>
<td>PP</td>
<td>0.479</td>
<td>-0.040</td>
<td>-12.10</td>
</tr>
<tr>
<td>PB1</td>
<td>0.572</td>
<td>0.006</td>
<td>92.92</td>
</tr>
<tr>
<td>PB1N</td>
<td>0.309</td>
<td>-0.359</td>
<td>-0.86</td>
</tr>
</tbody>
</table>

The ratio of $f_{I,A}^B$ to $f_{III,A}^B$ indicates the degree of uniaxiality or biaxiality in the orientation state. When it decreases to ‘1’, the orientation becomes more biaxial, while the uniaxial characteristics increase with increase of this ratio. It can be seen that PP, PB1 and PB1N exhibit increased uniaxial properties after the onset of crystallization. For the cases of PE, the orientation state becomes biaxial with the magnitudes of $f_{I,A}^B$ to $f_{III,A}^B$. 

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ratios being closer to ‘1’, compared with those in the melt state being 5.5, while the peculiar normal orientation of P4MP1 results in the ratio of $f_I^B$ to $f_{II}^B$ close to ‘1’ with negative sign.

A generalized linear relationship between the orientation state prior to and after the onset of crystallization has been investigated for the various polyolefins through the 4\textsuperscript{th}-order transformation tensor. It can be argued that in a phenomenological manner, the jumps of the crystalline orientation levels are reflected by the magnitudes of $S_{11}$ and $S_{13}$, and the modes of orientation may be explained by the ratios of $S_{11}$ and $S_{13}$. This approach, however, should be taken carefully since the nature of transformation tensor components is not only dependent on the level and the mode of the crystalline orientation, but also very closely related with the crystal structures and morphologies of polymers.

6.5 Conclusions

We investigated orientation and morphology development of various polyolefins injection molded at equivalent pressure and thermal condition in this chapter.

Deviations of the major principal axes from the machine directions were determined experimentally through the polarized light optical microscope (PLOM) with two crossed polarizers and through wide angle X-ray diffraction (WAXD) pole figures as well. From both methods, we observed essentially same distributions of extinction angle for semicrystalline polymers. The general behavior of the extinction angle in semicrystalline polyolefins showed some extent of variations in the transition layer and basically no variations in the mold surface and the core region, while amorphous
polystyrene (PS) showed maximum extinction angle at the mold surface and gradual decrease toward the core region. The magnitude of extinction angles among semicrystalline polyolefins ($5^\circ \sim 16^\circ$) was much smaller than that of PS, of which extinction angle showed maximum angle at $27^\circ$. This was attributed to the effect of rearrangement of molecular chains from crystallization.

The levels of average orientation determined from birefringence measurements were plotted along the principal axes determined previously. Relative orientation level from the considerations of intrinsic birefringence values seemed to be in order of

$$ PB1 \& PB1N > PP > PE >> PS $$

(6.36)

In case of P4MP1, there was experimental difficulties in determination of extinction angle distribution and understanding of relative orientation due to its very low intrinsic birefringence value.

From WAXD pole figure, we could construct orientation ellipses and determine crystalline orientation along the principal axes from the surface to the core of the molded polyolefin parts, including P4MP1. The relative crystalline orientation of c-axis was in order of

$$ P4MP1 \sim PB1 \& PB1N > PP > PE $$

(6.37)

which was in good agreement with the results found for melt spinning case in our research group [224]. For P4MP1, a phenomenon of normal orientation of c-axis was observed at high mold temperature injection molding. We concluded that this seems to be caused by the sufficient time given for P4MP1 to experience the crystalline relaxation, which is correlated to the main-chain translational mobility within the crystalline phase.
Morphological features as a function of depth along the mold were investigated. While PS showed no distinguishable crystalline morphology from its amorphous characteristics, various crystalline polyolefins exhibited well-defined micro sublayers, consisting of the skin layer, the transition layer and the typical spherulitic core. For P4MP1, however, study of crystalline morphology through PLOM seemed limited again with its low intrinsic birefringence. Even though, we could make presumptions from orientation measurements that P4MP1 would possess well-defined row structure in the surface of the mold, which is followed by transition layer of biaxially oriented texture and sheaf-like structures oriented along the normal direction of the mold at high mold temperature.

In the later part of this chapter, a phenomenological approach was proposed for establishing the relationship between the chain orientation of polymer melt and the crystalline orientation after the onset of crystallization. A generalized linear relationship was developed by the 4th-order orientation transformation tensor, $S_{ijkl}$ and its components for individual polyolefin were derived from the crystalline orientation factors and the Rheo-Optical rule for the polymer melt prior to the onset of crystallization, which would help to understand the jump of crystalline orientation level as well as the change of orientation mode compared with the prediction from the Rheo-Optical rule.
7.1 Conclusions

In this dissertation, we have made a comprehensive quantitative study of orientation and morphology development of various polyolefins in the injection molding process. This includes high density polyethylene (PE), isotactic polypropylene (PP), isotactic polybutene-1 (PB1), and isotactic poly(4-methyl pentene-1). We have considered (i) quiescent crystallization kinetics, (ii) effect of processing parameters on structure development, and (iii) changes in the mode of orientation during crystallization.

7.1.1 Quiescent Crystallization Kinetics

From studies of both isothermal and non-isothermal crystallization kinetics, the comparative order of crystallization rates was found from fast to slow

\[ \text{PE} > \text{P4MP1} > \text{PP} > \text{PB1} \]

This has been found to be in agreement with the results of earlier investigators [42,104].

7.1.2 Effect of Processing Parameters on the Structure Development

Crystal structures of injection molded polyolefin parts investigated through WAXD 20 scanning revealed that only PP exhibits polymorphism consisting of $\alpha$-monoclinic and $\beta$-hexagonal crystal, while PE, PB1 and P4MP1 do not show polymorphs instead
orthorhombic, tetragonal and hexagonal crystalline unit cells, respectively. The relative amount of \( \beta \)-hexagonal crystal of PP was found to vary through the thickness direction of the mold and increase with shear stress.

From birefringence and WAXD experiments, general features of orientation behaviors from the effect of processing parameters could be generally described as follows. Skin and transition layers with higher level of molecular orientation move closer to the mold wall as injection rate increases, while increase of packing pressure only influences the orientation in the core zone. As increase of mold temperature decreases cooling effect and brings skin and transition layers closer to the mold wall, increase of inlet melt temperature decreases relaxation time of polymer melt and results in thinner skin and transition layers with lower level of orientation.

7.1.3 General View of Polymer Chain Orientation

In order to specify the character and tilting of orientation, we developed a second order orientation tensor, \( O_{ij} \), inspired by the polarizability and the refractive index tensors. The component of \( O_{ij} \) describes the second moment of orientation distribution along \( ij \) direction as \( \cos \phi_i \cos \phi_j \), where \( \phi_i \) and \( \phi_j \) represent the angles between a chain axis and \( i \) and \( j \) principal axes, and this was applied to both flowing melts and solidified parts.

The orientation tensors for the various injection molded parts studied differed considerably. The principal axes are in different directions and the ellipsoid shape vary. For glassy polystyrene, the major principal axis has a extinction angle with the flow direction which is a maximum (~27°) around the mold surface and decreases to zero in
the core region. For the polyolefins, the principal axis of orientation is nearly parallel to the flow direction in the region close to the mold wall and in the core of the mold with the maximum extinction angles ranging from 5° to 16° to the flow direction in the intermediate region.

7.1.4 Change of Mode and Magnitude in Orientation

Stress induced birefringence in amorphous polymers was first studied by Kuhn and Grun [240] in conjunction with the theory of rubber elasticity, and this concept was later extended to flowing polymer solutions and melts by Lodge [241]. In order to determine the stress fields, the Rheo-Optical rule, making quantitative use of this behavior [242], has been applied to birefringence of the injection molded amorphous polystyrene parts in our experiments, which was processed at the same injection pressure as applied to the various polyolefins. Through presumably equivalent flow stress during mold filling associated with the constant injection pressure and cooling stress set up from considerations of inlet melt and mold temperatures with melting temperature of each polyolefin, it was possible to carry out objective comparison of orientation and morphology development among various polyolefins.

The modes of crystalline orientation after the onset of crystallization changed in a different manner for different polymers. Especially in the region close to the mold surface, PP and PB1 distinguished themselves from PE and P4MP1 in that the formers showed well-defined uniaxial orientation characteristics, while PE and P4MP1 exhibited the characteristics of largely biaxial orientation in the plane perpendicular to the thickness and the flow directions, respectively. As we approach deeper to the core region, the
orientation becomes randomly distributed for all the polyolefins investigated except P4MP1, which exhibited a very peculiar phenomenon of c-axis normal orientation to the mold surface at high mold temperature injection molding, which might be attributed to the main-chain translational mobility within the crystalline phase.

Along the principal axes obtained, the relative levels of crystalline orientation from the surface to the core of the molded polyolefin parts were determined and with considerations of relaxation behaviors, the crystalline orientation of c-axis along the flow direction was found to be in order of

\[
P4MP1 > PB1 > PP > PE
\]

and it is notable that this ordering is in good agreement with that in the melt spinning case by Choi and White [224].

7.1.5 Phenomenological Approach for Orientation Transformation

With efforts to establish the relationship between the chain orientation of polymer melt and the crystalline orientation after the onset of crystallization, a phenomenological approach was proposed. In this approach, a generalized linear relationship between two orientation tensors, \( O_{ij}^C \) and \( O_{kl}^A \), representing the polymer melt state and crystallized state, respectively, was developed by the 4\(^{\text{th}}\)-order orientation transformation tensor, \( S_{ijkl} \), as

\[
O_{ij}^C = S_{ijkl}O_{kl}^A,
\]

which reduces to

\[
O_{ij}^C = S_{ij}O_{j}^A
\]

because of the symmetry of the \( O_{ij} \) tensor.

The components of \( S_{ij} \) derived from the relationship between the crystalline orientation factors determined by WAXD pole figures and the orientation in the melt state prior to the onset of crystallization by using the Rheo-Optical rule, represent such
characteristics of different polyolefins as the jump of crystalline orientation level and the change of orientation mode compared with the prediction from the Rheo-Optical rule.

7.2 Recommendations

It is recommended to extend the methodology of the present study to other classes of polymers, which may include (a) isotactic and syndiotactic forms of polyolefins and polystyrenes and (b) polyamides, in which additional considerations should be taken for the role of hydrogen bonding.

Quantitative modeling of crystalline orientation in injection molding of polyolefins and comparison between theoretical and experimental modeling are also recommended, which should be accompanied by improvements in understanding of shear flow induced crystallization as well as relaxation behaviors of the various polyolefins.
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