

The effect of polyolefins' structure on its processing properties

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ABSTRAKT

Tato studie zkoumá vlastnosti zpracování izotaktického polybuten-1 (iPB-1) a objasňuje složitou roli přímých elektrických polí a disperze a distribuce přísad při modulaci rychlosti fázového přechodu (II→I). Odhaluje silnou korelaci mezi výjimečnou disperzí a distribucí přísad a rychlejšími fázovými přechody, což naznačuje zvýšení účinnosti nukleace. Nicméně určité přísady, jako je MnZn ferrit, se od tohoto trendu odchyľují, což ukazuje na specifické účinky přísad na kinetiku fázového přechodu. Studie také zdůrazňuje dopad přirozeného stárnutí a aplikace síly na dynamiku fázového přechodu a složitý vztah mezi intenzitou elektrického pole, jeho aplikací během chlazení a rychlostí fázového přechodu. Tato zjištění poskytují nuancované pochopení proměnných ovlivňujících fázové přechody iPB-1 a zdůrazňují potřebu dalšího průzkumu v této oblasti.

Klíčová slova: Izotaktický polybuten-1 (iPB-1), Rychlost fázového přechodu, Přímá elektrická pole, Disperze a distribuce přísad.

ABSTRACT

Investigating the processing attributes of isotactic polybutene-1 (iPB-1), this study elucidates the complex role of direct electric fields and additive dispersion and distribution in modulating the phase transition rate (II→I). It unveils a strong correlation between superior additive dispersion and distribution and faster phase transitions, suggesting increased nucleation efficiency. However, certain additives such as MnZn ferrite deviate from this trend, indicating additive-specific effects on phase transition kinetics. The study also highlights the impact of natural aging and force application on phase transition dynamics and the intricate relationship between electric field intensity, its application during cooling, and the phase transition rate. These findings provide a nuanced understanding of the variables influencing iPB-1 phase transitions and underscore the need for further exploration in this domain.

Keywords: Isotactic polybutene-1 (iPB-1), Phase transition rate, Direct electric fields, Additive dispersion, and distribution.

I would like to express my deepest gratitude to my family for their unwavering love, encouragement, and support throughout my entire academic journey. Their constant belief in my abilities and their sacrifices have been instrumental in shaping the person I am today. I am genuinely grateful for their enduring presence in my life.

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"Experience without theory is blind, but theory without experience is mere intellectual play."

- Immanuel Kant

I hereby declare that the print version of my Master's thesis and the electronic version of my thesis deposited in the IS/STAG system are identical.

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INTRODUCTION

Isotactic polybutene-1, a polymer notable for its unique phase transition characteristics, has been an area of significant interest within material research. The dynamic nature of its phase transition from form II to form I presents an intriguing research landscape, given the multitude of influencing factors such as direct electric fields, additive dispersion and distribution, and natural aging.

The crux of this study lies in the exploration of these variables, with a particular focus on their interplay with the phase transition rate. The analytical tools of Wide-Angle X-ray Scattering and Differential Scanning Calorimetry have been instrumental in elucidating these relationships, shedding light on additive-specific effects and the role of processing conditions in phase transition kinetics.

Natural aging emerges as a potential modifier of phase transition dynamics, adding complexity to our understanding of these processes. Early indications suggest that significant changes in the material's properties could occur as a result of natural aging, despite the limitations in thoroughly evaluating this effect.

Further, the influence of external factors, such as the application of electric fields and forces during the melting process, is examined. Preliminary findings indicate these factors could facilitate the phase transition, with the electric field intensity and application timing playing crucial roles.

I. THEORY

1 SYNTHETIC POLYMERS

Polymers are materials in which a large molecule (macromolecule) is built from many small, relatively simple subunits called "monomers". Thus, these monomers represent a chemical building block that allows extraordinary variability of structures and properties of the resulting materials. The main chain of a macromolecule, also called the "backbone", is usually made of carbon atoms, but other elements such as oxygen, nitrogen, silicon, and others may be present. Other atoms, such as carbon, hydrogen, oxygen, nitrogen, chlorine, fluorine, etc., bind to the atoms that form the chain's backbone, resulting in a complex structure. The chemical structure of macromolecules determines all the basic properties of polymers: mechanical, thermal, chemical, and electrical, flammability, degree of wettability, and others. [1][2]

The properties of unfilled polymer materials reflect their chemical structure, the molecular composition (shape and length of the macromolecules and the magnitude of the forces between the molecules), and the supramolecular structure, which is related to the arrangement of the macromolecules relative to each other. For this reason, this chapter will discuss in detail the polymers' constitution, configuration, and conformation. [2]

1.1 Polymer's Structure

Polymers are substances characterized by their basic units being extremely large molecules - macromolecules. [3]

1.1.1 Macromolecules

Macromolecules are formed by joining a large number of repeating parts - mers. Mers are the residues from initial molecules - monomers. A small number of joined mers are referred to as - oligomer, and a large number as - polymer. Depending on the method of formation, it may be further referred to as polycondensate, polyadduct, or polymerate. Macromolecules can be linear, branched, and in exceptional cases, cross-linked. Figure 2 presents linear, branched, and cross-linked polymer chain structures. [3]

When two types of monomers are used, copolymers are formed. When a trifunctional unit is used, a graft copolymer can also be formed. Depending on the alignment of the monomers in the macromolecule, three types of copolymers can be recognized (see Figure 1). [3]

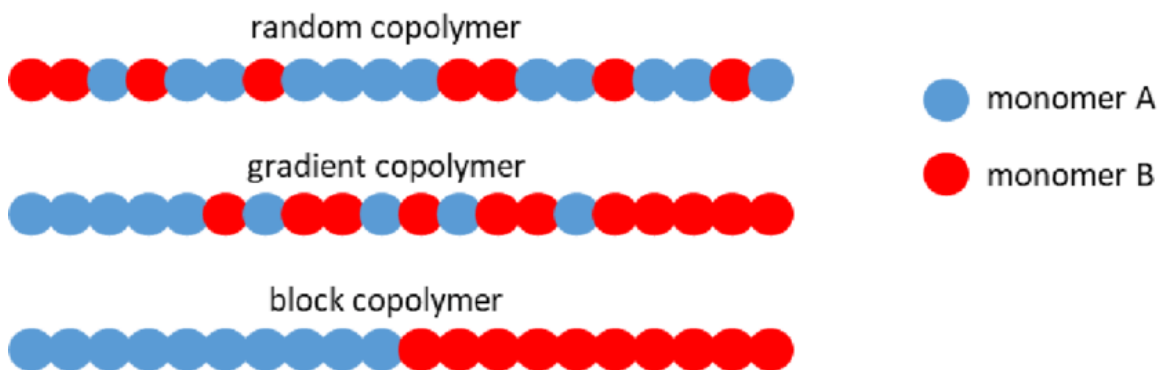


Figure 1 Scheme of random, gradient, and block copolymer [4]

In addition, in the case of a non-symmetric bifunctional unit (where we find the head and the tail), we still recognize the connection of bifunctional units: head-to-tail, tail-to-tail, and head-to-head. [3]

1.1.2 Polymer's Constitution

The joining of bifunctional monomer molecules in a chain growth polymerization produces the simplest type of macromolecule - linear macromolecules. Macromolecules are linear because each monomeric unit is connected to only two adjacent units. However, they are not linear in the sense of straightforwardness. As a result of the rotation of atoms around simple bonds, macromolecules can take on different conformations. The most energetically favorable and, therefore, statistically most likely is the occurrence of macromolecules in the form of a ball. Macromolecules that possess side chains are known as branched. They are formed by the polymerization of three or more functional monomers but can also result from a side reaction in the polymerization of a bifunctional monomer. The branched macromolecule is fully characterized by the degree of polymerization number and length of side chains. With increasing length and number of side chains in branched macromolecules, the probability of their interconnection increases. A cross-linked polymer is formed if all chains in a three-dimensional space are bonded together. Thus, such a polymer is characterized by the density of the network and the length of the chains between the cross-linking sites. A three-dimensional polymer network can be formed not only by polymerizing three or more functional monomers but also by bonding linear or branched macromolecules, such as during the vulcanization of rubber. Undesired cross-linking of linear or branched polymers can occur at high enough temperatures and due to side reactions. [6]

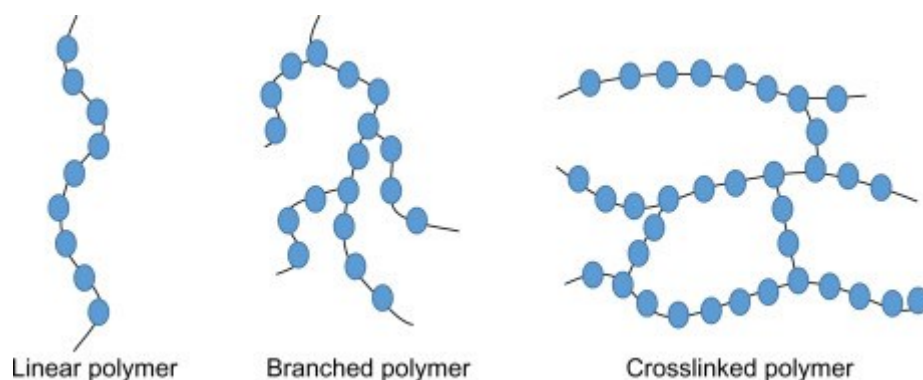


Figure 2 Schematic representation of linear, branched, and cross-linked polymers [5]

Polymers whose macromolecules contain only one monomeric unit type are called homopolymers. The polymerization of two or more types of monomers results in copolymers. [6]

1.1.3 Polymer's Configuration

Configuration determines the relative arrangements of atoms and substituents in macromolecules. This arrangement is chemically stable and cannot be changed without breaking a chemical bond. The cause of the spacial isometry is both the tetrahedral arrangement of the substituents on the asymmetric sp^3 carbon atom and the planar arrangement of the substituents on the carbon atom from which the double bond emerges. [6]

The arrangement of stereoisomeric centres in the main chains of macromolecules is called tacticity. Polymers in which the macromolecules have a high degree of orderliness in the arrangement of the stereoisomeric centres are referred to as tactical. [3][6]

Thus, these are cases where, with the same composition and with the same configuration of the mer, some of its atoms or groups occupy different positions concerning its centre of steric isomerism. For synthetic polymers, the stereocentre is often a double bond. When repeated regularly along the chain, this type of steric isomerism is also called cis- or trans-tacticity. Another center of steric isomerism is a C-atom with two different substituents. Tacticity is established if one of the substituents is placed in structural units (mers) along the chain according to some rule. [3]

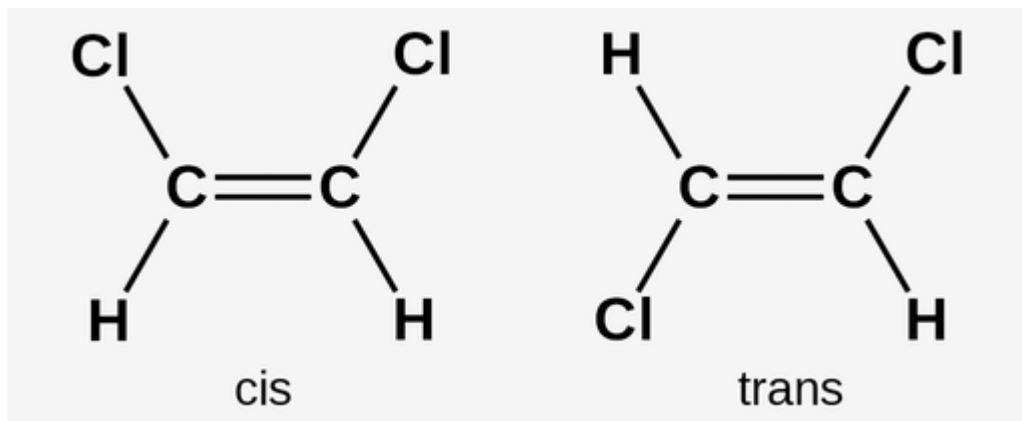


Figure 3 Cis and trans isomers of dichloroethene [7]

1.1.3.1 *Isotactic Configuration*

Isotactic polymers are those polymers which have all stereosymmetric centres in the macromolecules of the same configuration. The isotactic polymer has a higher melting temperature and mechanical strength than the other configurations' polymers. These properties make it the most commercially desirable configuration. [6][8]

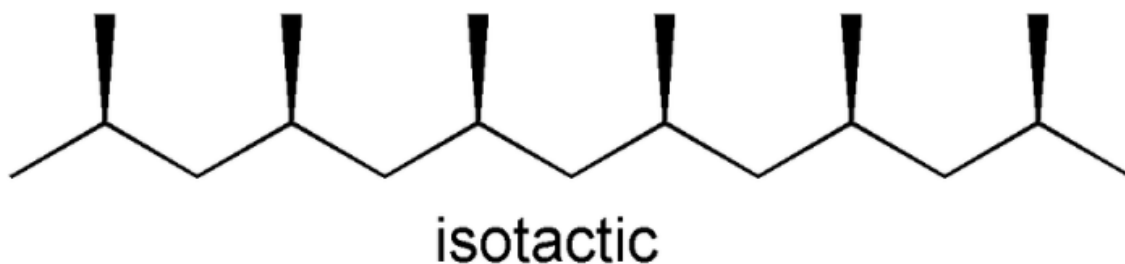


Figure 4 Scheme of isotactic configuration [9]

1.1.3.2 *Syndiotactic Configuration*

Syndiotactic polymers are characterized by alternating configurations of stereoisomeric centres in macromolecules where the substituent is alternately above and below the spine of the carbon chain. [6][8]

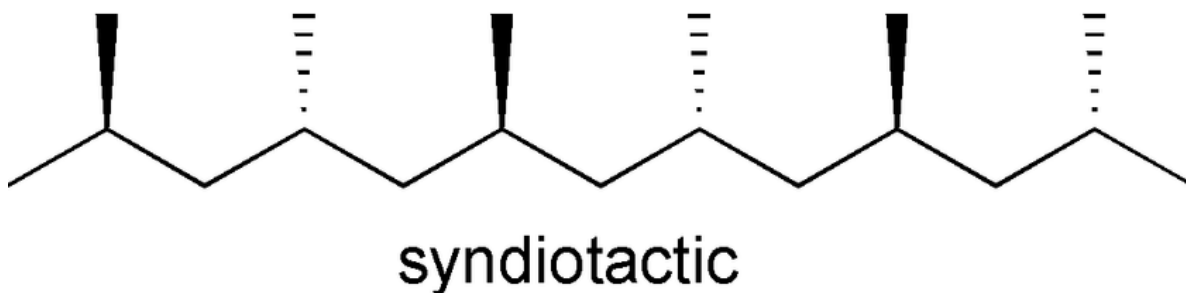


Figure 5 Scheme of syndiotactic configuration [9]

1.1.3.3 Atactic Configuration

Isotactic polymers do not exhibit a uniform distribution, as is the case of syndiotactic and isotactic polymers. Their arrangement is, therefore, entirely coincidental. [6][8]

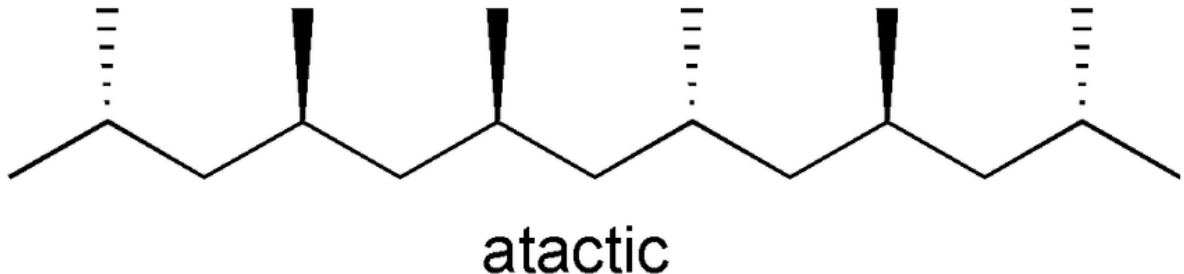


Figure 6 Scheme of atactic configuration [9]

1.2 Conformation of Polymers

The configuration of a polymer refers to the spatial arrangement of its constituent monomer units and can significantly impact its properties. Individual arrangements are called conformation; a chain can adopt many different conformations. However, the above situation can only occur in the case of entirely free rotations. In reality, rotational position changes are met with resistance at certain angles, which is associated with overcoming energy barriers. [3]

1.2.1 Conformation of crystalline Polymers

Only those conformations that allow regular side-by-side arrangement of at least a part of the chains can transition to the crystalline state. At the same time, they must have minimum internal energy in this state (spontaneous formation of the crystal structure). This will be determined by the following factors acting simultaneously:

- The geometric shape (configuration) of the chain
- Rotation around the bonds allows transition to the desired conformation. It is affected by the values of the van der Waals radius of the atoms and the valence angles.
- Interaction along the chain and across the chain. [3]

1.3 Morphology of Polymers

Morphology is the science that deals with the structure. In the case of polymers, it can be stated that their chains may commonly be found in entirely random conformations, where they are not able to arrange themselves regularly in space next to each other, nor are they able to form any structure, and are therefore called amorphous. When they are capable of forming regular upright conformations, they also arrange themselves regularly in space to form structures similar to low molecular weight crystalline substances. Polymers with this ability to chain are therefore called crystalline. Realistically, there is no pure crystalline state of a polymer. [3]

1.3.1 Amorphous Phase

The amorphous state is characterized by very random conformations of chains, which due to energetic reasons, are rolled up into various bulky, statistical clumps depending on the conditions. Its size varies with conditions, the most important of which are temperature and the presence of certain low molecular-weight substances (solvents, plasticizers). Mechanical stress at higher temperatures in the melt further alters its dimensions and shape. With increasing stresses in the melt flow, the bulks develop to the limit of the chain's stretched state. Both in the solid state and in the resting melt, it can be assumed that the bulks of the individual chains more or less interpenetrate each other. Chain entanglement affects the properties in the solid state and in the melt. There are conditions where even an otherwise crystallizable polymer can be prepared in a purely amorphous, solid state - for example, superfast melt cooling. [3]



Figure 7 Scheme of Amorphous Phase [10]

1.3.2 Crystalline Phase

There is no purely crystalline polymer. For this reason, they are referred to as semi-crystalline polymers. In the case of semi-crystalline polymers, one can distinguish between an amorphous and a crystalline phase, which may be further subdivided in space. The phase composition in space depends to some extent on the content of the crystalline phase. [3]

- Only clusters of parallel-oriented chain segments can form at low crystalline phase contents, which "float" in an amorphous phase.
- At higher to high crystalline phase content, we observe the formation of crystalline, planar formations, which one can call lamellae. A single chain can be gradually stacked into multiple lamellae one after the other while passing through the interlamellar space in a non-orderly pattern, which always remains amorphous. [3]

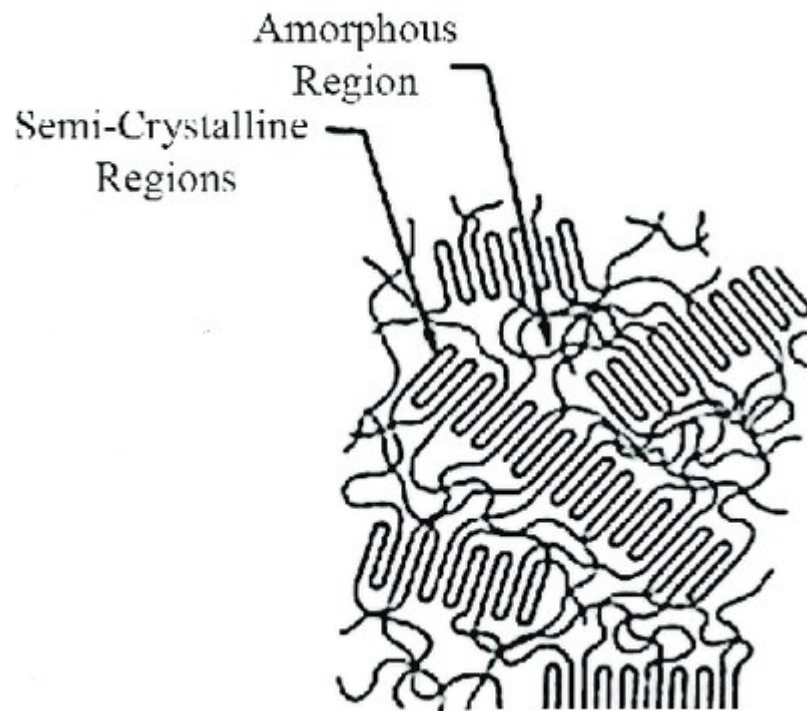


Figure 8 Scheme of the semi-crystalline polymer [10]

The crystalline phase can never reach 100%. There is always a certain percentage of amorphous fraction in a single crystal. The amorphous fraction primarily comprises chain bends, misaligned ends, branches, portions of the interpenetrating molecules, and overall dislocations of the crystal lattice. [3]

2 POLYBUTENE-1

Isotactic polybutene-1 (iPB-1) was discovered and synthesized for the first time in the year 1954 by Giulio Natta and Karl Ziegler for the synthetization stereo-specific catalysts (known as Ziegler-Natta catalysts) were used for the polymerization, resulting in the production of a highly isotactic polymer. Despite its excellent mechanical properties and excellent chemical resistance, industrial production of isotactic polybutene-1 did not begin for many decades after its discovery, as was the case of polyethylene and polypropylene. [11][12]

Industrial production of iPB-1 began in the early 1970s in Germany; however, it was soon closed down. In the mid-1970s, another production appeared in Texas (USA) and was closed in a few years. After the 1980s, the production of iPB-1 is slowly rising. For example, one of the highest producers in the 1980s, company Werke Huels (Germany), was synthesizing around 12 000 tuns annually, and as of 2021, annual production of iPB-1 at company LyondellBasell (Netherland) – one of biggest producers now - is around 50 000 tuns. [11-14]

2.1 1-Butene

1-Butene is a linear alpha olefin with the chemical formula C_4H_8 . It is a colorless gas with a mild odor and is flammable. It is used primarily as a monomer in the production of polybutene-1. It can be produced by the catalytic cracking of hydrocarbons, such as naphtha and gas oil, or by the dehydration of butanol. It is also produced as a byproduct during ethylene and propylene production. [11,15,16]

2.2 Isotactic Polybutene-1

Isotactic polybutene-1 (iPB-1) is a semi-crystalline thermoplastic polymer synthesized through the polymerization of butene-1 monomer units. As a highly isotactic polymer, the butene-1 monomer units within the polymer chain exhibit a consistent orientation concerning the polymer's backbone. This consistency leads to a highly organized, crystalline structure, endowing the material with distinct properties [9,11,17].

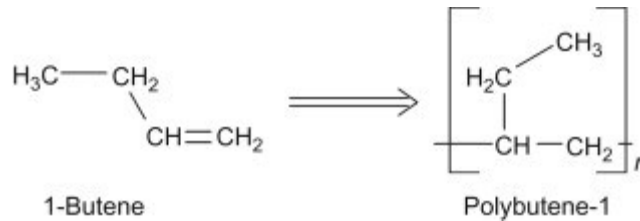


Figure 9 Structure of 1-butene monomer and PB-1 polymer [18]

Owing to its elevated melting point and exceptional resistance to deformation, iPB-1 is well-suited for a range of applications, such as piping systems, packaging materials, and films. Its impressive resistance to chemical degradation also makes it a prime candidate for use in harsh chemical conditions [11][17]. A notable characteristic of iPB-1 is its amenability to various processing techniques, including injection molding, blow molding, and extrusion. This adaptability makes it an attractive option for manufacturers seeking a material that can be effortlessly shaped into intricate designs [11][17]. The predominant method of producing iPB-1 involves the employment of a Ziegler-Natta catalyst system, which requires a transition metal compound and an organoaluminum compound to function as co-catalysts. The Ziegler-Natta catalyst system coordinates the monomer units (butene-1 in this instance) to the catalyst's metal center. This coordination enables the monomer units to undergo several reactions, such as insertion into the polymer chain and chain termination, ultimately leading to the formation of the polymer. The properties of the resultant iPB-1 polymer can be influenced by multiple factors, including the catalyst type and quantity, reaction temperature and pressure, and solvent selection [9,11,17].

2.3 The crystalline structure of Polybutene-1

Several researchers have investigated the polymorphic behavior of isotactic poly-1-butene, as reported in references [19-21]. Five distinct crystalline phases of poly-1-butene have been identified: phases I, II, III, I', and II'. The phases of primary practical significance are I and II.

Poly-1-butene initially crystallizes from a melt into a tetragonal crystal phase II, which has a square shape and is characterized by an 11/3 helical conformation. This crystal form has a melting temperature range of 128 - 131°C. Over time, phase II gradually and spontaneously transforms into a trigonal crystal phase I, which has a rhombic shape and a 3/1 helical conformation. The melting temperature range of phase I is 121 - 141°C. As the transition from phase II to phase I occurs, the macromolecules become straighter, leading to a 14% elongation of the macromolecules and a 10% reduction in the cross-sectional area [21].

When poly-1-butene is crystallized from various solvents or at temperatures up to 100°C, an orthorhombic crystal phase III with a rectangular shape, a 4/1 helical conformation, and a melting temperature of around 96°C can be formed. Although phase III is stable at room temperature, it transforms into phase II as the temperature approaches the melting point. Subsequently, phase II transforms to phase I [11][21].

The fourth crystal phase, I', is formed under high pressure and from a suitable solvent during crystallization. It differs from phase I in its crystal structure, which is a non-twinned hexagonal structure. The melting temperature range of phase I' is lower than that of phase I, falling between 95 and 100°C.

Finally, the fifth crystal phase, II', can be formed by high-pressure crystallization under carefully controlled conditions.

In general, phases II and III are less stable than phase I over the entire temperature range due to the higher positional energy of the polymer chain particles [11].

2.4 Phase transitions of iPB-1

Isotactic polybutene-1 is a polymer with good mechanical properties, excellent elastic resilience, good chemical resistance, and can withstand thermal stress well. Unfortunately, its industrial use is influenced by the relatively slow transition from the tetragonal, unstable crystalline phase II to the physically stable and mechanically superior crystalline phase I. The unstable tetragonal phase II is formed during the melt's crystallization and spontaneously transforms into the stable form I. The most common phases are I, II, and III, which have different melting temperatures, enthalpies [22][23], and X-ray diffraction spectra. The image x was taken using transmission electron microscopy (TEM). [21]

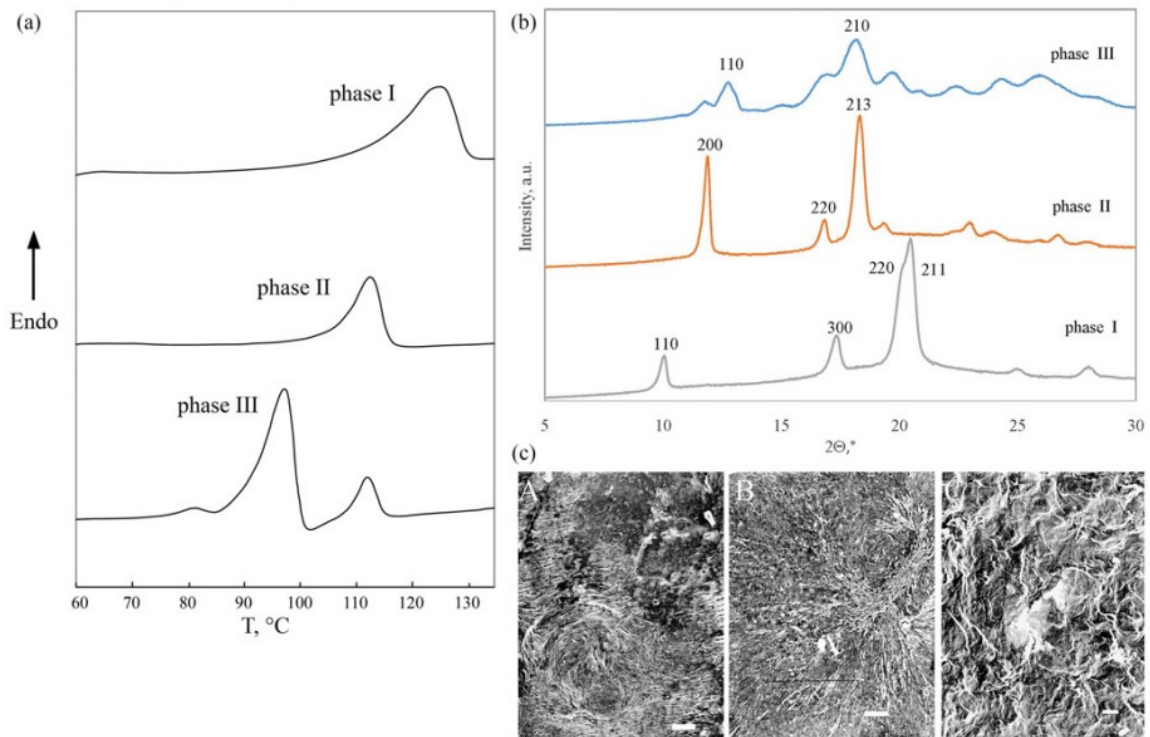


Figure 10 DSC scans (1A), X-ray diffraction spectra (1B), and TEM images (1C) of the three primary crystal forms of isotactic polybutene -1 (I, II, III) [21]

Figure 10A illustrates that phase I is thermodynamically more stable than the other crystalline phases across the entire temperature range. The transmission electron microscopy image in Figure 10C shows typical lamellar and spherulitic structures of phases I, II, and III. [21]

From a practical perspective, the most important and extensively studied phase transition is the II → I phase transformation. The transformation from phase II to phase I initiates with the movement of the polymer's side chains. The polymorphic transition of phases II → I consists of two parts, the first of which involves slow nucleation and rapid growth, while the second involves extremely slow secondary nucleation and growth. The growth rate of crystalline phases has been investigated by Yamashita and Takahashi [24], who found that at a temperature of 75°C, the growth rate of phase I crystals is about one-hundredth of that of phase II crystals. Therefore, it can be inferred that all crystals were originally in phase II [20][21].

The transition from phase II to phase I is associated with an increase in density, a reduction in the volume of the crystalline phase, and a segmental spatial reorganization. Phase I crystals' volume decreases by approximately 4% compared to phase II crystals, which increases the stress on the connected segments of the amorphous chain at the amorphous crystal interface [21].

Three types of the II → I phase transformation occurs depending on the form of the transformation nucleus. These types are designated as P (plus), N (neutral), and M (minus). The P-type is faster than the standard transformation, while the N-type represents the standard transformation from phase II to I. The M-type involves an induction period that slows the phase transition's beginning and is, therefore, slower than the previous types. [21]

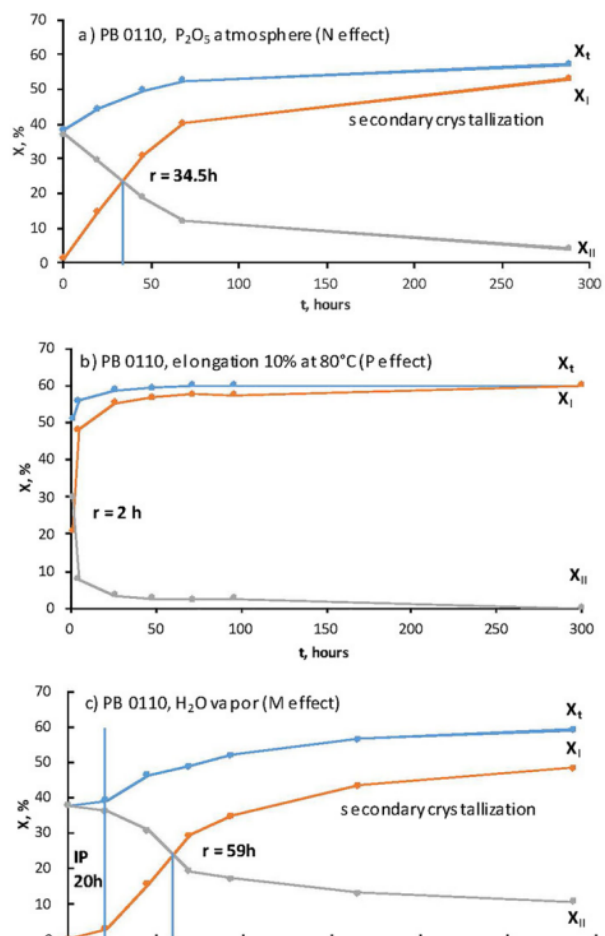


Figure 11 Example of transformation phases that can occur [21]

2.4.1.1 The influence of molecular weight on the phase transition II → I

The influence of molecular weight on the phase transition II → I has received significant attention. Studies by Foglia [25] and Chaua et al. [26] have shown that the phase transformation rate increases with decreasing chain length. Samples with shorter chain molecular weight contain a relatively higher amount of mobile end groups per unit volume, facilitating the developmental phase's nucleation and growth processes. [21][25][26]

2.4.1.2 The influence of copolymerization on the phase transition II → I

The effect of copolymerization on the II → I phase transformation has been extensively studied. Kopp et al. [20] found that the phase transformation process is accelerated by copolymerization with, for example, ethylene and propylene. Stolter et al. [27][28] demonstrated that ethylene co-units in copolymers of butene-1/ethylene are mostly excluded from the crystallization of phase II, and during the II → I phase transformation, these ethylene units are transferred to the amorphous phase. Liu et al. [29] confirmed that ethylene copolymers suppress crystallization and soften the amorphous phase, thus accelerating the II → I phase transition. Significant acceleration was observed in samples with 4.3% and higher ethylene fractions. This acceleration was attributed to the heterogeneity of segmental mobility, which facilitates crystal growth and defects accumulating on the surface of the bend, causing internal stress for nucleation acceleration. [21][27-29]

2.4.1.3 The influence of the cooling rate of the melt on the phase transition II → I

The study by M. Kaszonyiová and F. Rybníkář [21] investigated the effect of cooling rate during the crystallization of melted samples on the transformation from phase II to phase I. The results showed that rapid cooling of the melt increased the II → I phase transition rate. Specifically, samples that were rapidly cooled (immediately covered with a separating film after melting and placed in room temperature water) exhibited a phase transition half-life of 37 hours (transformation type N), whereas samples that were freely cooled at room temperature had a half-life of 59 hours (transformation type M) [21]

2.4.1.4 *The effect of additives on the phase transition II → I*

In the majority of cases, recrystallization entails heterogeneous nucleation. Consequently, numerous studies [21][30] have explored the impact of nucleating agents on the phase transition from II to I. A crystallographic relationship needs to exist between the polymer's crystal structure and the additives containing nucleating centers. Rubin [30] discovered that chloronaphthalene and diphenyl ether expedited the phase transition from II to I, while glycerol and carbon black did not impact the transition. Kaszonyiová and Rybníkář [21] found that potassium chloride accelerated the II to I phase transition from the initial 36 hours to 24 hours [21][30].

Crystal-based additives can serve as fillers to enhance the mechanical properties of iPB-1. Montmorillonite has been shown to disrupt iPB-1's morphological arrangement, thereby hastening the phase transition from II to I, as documented by Causin et al. [31] and Wanjal and Joga [32]. Causin et al. [33] further identified montmorillonite as an effective additive for improving the mechanical and thermal properties of iPB-1 [21] [31-33].

Wanjal and Joga [34] determined that the inclusion of multi-walled carbon nanotubes (MWCNTs) accelerated the phase transition from II to I, attributing this to the reduction in amorphous content and the increased nucleation of phase I due to the disorganized morphology of the crystals [21][34].

Zhang et al. [29] examined aluminum silicate's and magnesium silicate's effects on the phase transition from II to I. In both instances, the transition was expedited. The acceleration in the case of magnesium silicate was attributed to its lattice match with the crystal structure of phase I, while the acceleration in the case of aluminum silicate was less pronounced due to the lack of a lattice match [21][29].

The studies mentioned above have investigated the influence of various additives on the phase transition from II to I in iPB-1. However, it is essential to note that none of the referenced papers [21] [29-34] have specifically addressed the distribution and dispersion of the additives within the iPB-1 matrix. This research gap could be crucial for comprehending the complete impact of additives on phase transitions and their potential effects on material performance. In the context of this thesis, examining the distribution and dispersion of additives may offer a more thorough understanding of the phase transition from II to I in iPB-1, revealing new research possibilities and potential applications.

2.4.1.5 The effect of electrical field on the phase transition II \rightarrow I

Although significant research has been conducted on phase transitions in isotactic polybutene-1 (iPB-1), there is a conspicuous lack of studies investigating the impact of electric fields on these transitions. The unexplored nature of this subject not only results in a considerable gap in the comprehension of iPB-1's phase behavior but also offers an opportunity for further inquiry in the practical portion of this Master's thesis.

The dearth of research regarding the influence of electric fields on iPB-1 phase transitions prompts several questions concerning the possible ramifications of such effects. Delving into this subject could uncover new properties and uses for iPB-1 and shed light on the underlying mechanisms governing its phase behavior. By addressing this knowledge deficit, the practical aspect of this thesis aims to augment the scientific community's understanding of iPB-1 and expand its potential for industrial applications.

2.4.1.6 *The effect of natural aging on the phase transition II → I*

The impact of natural long-term aging on isotactic polybutene-1 (iPB-1) has been thoroughly examined [35-39], offering insights into the alterations that occur in this polymer over time. One of the primary consequences of aging on iPB-1 is a reduction in crystallinity. Even after 17 years, an unstable phase II remains detectable in the polymer samples. This unstable phase may be ascribed to changes in the polymer's structure and morphology over time [35].

Fourier Transform Infrared (FTIR) analysis was employed to explore the aging process, revealing that the primary effect of aging on iPB-1 was an alteration in the ratio of methyl/methylene functional groups. This change suggests a potential cleavage of the side chains, resulting in diminished geometric regularity of the molecular chain. The reduced regularity of the molecular chain impedes the spontaneous phase transformation, consequently slowing down the process [35].

Additionally, it was noted that the separation of side chains led to the formation of groups that further decelerated the phase transformation. These groups can be eliminated through repeated melting of the polymer sample. The study [35] also determined that the structural changes in the iPB-1 polymer during the aging process are primarily associated with chain segmental conformational changes. This finding highlights the importance of molecular conformation in the phase transformation behavior of iPB-1 [35].

The effect of aging on the phase transformation rate and the degree of crystallinity varied among samples. Some samples demonstrated a significant increase in half-time values, while others exhibited only minor differences. Intriguingly, it was found that following the third melting of aged samples, the induction period vanished, and the type of phase transition shifted from M to N. This observation implies that repeated melting can eliminate defects that obstruct the formation of nuclei and modify the transformation behavior of the polymer [35].

3 METHODS OF CRYSTALLINITY MEASUREMENT

Various measurement methods can be employed to determine polymer crystallinity, such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Fourier-transform infrared spectroscopy (FTIR). XRD is an effective technique for obtaining in-depth information about polymers' crystal structure and morphology. DSC can be utilized to ascertain the degree of crystallinity, melting temperature, and heat of the fusion of polymers. FTIR is a valuable tool for examining the molecular structure and orientation of polymer crystals. When used in conjunction, these techniques can offer a comprehensive understanding of the crystalline properties of polymeric materials [40-44].

3.1 X-Ray Diffraction

X-ray diffraction (XRD) is an effective technique for examining the structure of polymeric materials. It can be employed to determine the degree of crystallinity, crystallite size, and crystal orientation. By analyzing the diffraction pattern, XRD can offer detailed information about the crystal structure of the material [40][41].

3.1.1 X-Ray

X-rays, a form of electromagnetic radiation, were discovered by Wilhelm Conrad Roentgen in 1895. They possess a shorter wavelength than visible light and can penetrate various materials, including soft tissue and bone, making them valuable in numerous applications such as medical imaging, non-destructive testing, and crystallography.

The generation of X-rays typically involves bombarding a metal target, like tungsten, with high-energy electrons in a vacuum. This process prompts the metal atoms to emit X-rays as they lose energy, which can then be detected by an appropriate instrument.

X-rays interact with matter primarily through two processes: absorption and scattering. When X-rays come into contact with atoms in a material, they can either be absorbed by the atoms or scattered in different directions. The extent of absorption and scattering depends on the X-rays' energy and the material's properties, such as its density and atomic structure.

X-ray crystallography is another crucial application of X-rays. It entails directing X-rays at a crystal to examine the crystal's atomic structure. As X-rays are diffracted by the atoms within the crystal, they produce a diffraction pattern that can be analyzed to determine the structure of the crystal [44].

3.1.2 XRD

X-ray diffraction (XRD) is an essential experimental technique widely used in the field of material science, and more specifically in the study of polymeric materials, to decipher the underlying crystal structure. The crystalline structure of a material can be visualized as an infinite three-dimensional lattice capable of accommodating an unlimited number of equidistant planes with varying orientations and distances. Bragg's law is a fundamental principle governing the interaction of monochromatic X-ray radiation with these lattice planes. Bragg's law stipulates the specific angle of incidence at which X-ray radiation will undergo constructive interference, resulting in the reflection of the incident radiation. [41-43]

Imagine a scenario in which a beam of monochromatic X-ray radiation is aimed at a single crystal. In this situation, no X-ray reflection would be observed, as the Bragg condition would not be satisfied. However, if a multitude of crystals, randomly oriented concerning the incident beam, were present, there would invariably be a specific subset of crystals oriented such that the Bragg condition is satisfied, thereby leading to X-ray reflections. Given a large number of randomly oriented crystals, reflections can occur from all possible lattice planes, provided their interplanar distance is greater than half the wavelength of the monochromatic X-ray radiation. For the evaluation of reflections in polycrystalline materials, it is paramount to use monochromatic radiation. [41-43]

When investigating the structure of polymeric materials, the focus is generally on interplanar distances ranging from 1 to 20 Ångströms (Å). These interplanar distances dictate the required wavelength of X-ray radiation to be used. However, X-ray radiation with a wavelength longer than 2 Å is highly absorbed by the atmosphere; thus, wavelengths shorter than 2 Å are typically employed in practice. This X-ray wavelength corresponds to the characteristic X-ray radiation of certain metals, such as Silver (Ag), Molybdenum (Mo), Copper (Cu), Iron (Fe), and Chromium (Cr). [41-43]

The interaction of X-ray radiation with individual planes of atoms in a crystal leads to the formation of a system of cones of reflected X-ray beams, which are symmetrically arranged around the primary beam. When these cones are captured on a flat photographic film, they generate diffraction patterns that appear as concentric circles. The evaluation of the reflection angle, necessary for the computation of interplanar distances 'd' using Bragg's law, and the determination of the intensity of individual reflections, are typically performed using radial photometric measurements of the X-ray film's density. In instances where direct registration of scattered radiation is possible, the need for photographic registration and photometry can be bypassed. [41-43]

In addition to these basic principles, more sophisticated techniques based on X-ray diffraction, such as Powder X-ray Diffraction (PXRD) and Single Crystal X-ray Diffraction (SXRD), provide even more detailed insights into the crystal structure of polymers. PXRD is particularly useful for studying the average crystal structure over a large number of crystallites, while SXRD allows for the determination of the exact atomic arrangement within a single crystal. Furthermore, the X-ray diffraction technique is also applicable in studying the thermal behavior of polymers, such as thermal expansion and phase transitions, by performing temperature-dependent measurements. [41-43]

3.2 DSC

Differential Scanning Calorimetry (DSC) is an indispensable tool in the toolbox of materials scientists, particularly those working with polymeric materials. The technique, which involves the quantification of heat fluxes absorbed or released by a sample under controlled thermal conditions, provides critical insights into the thermal behavior and related properties of polymers. These properties include, but are not limited to, glass transition temperatures, melting points, crystallization behavior, and thermal stability. DSC has found wide applications in the formulation, characterization, and quality assurance of polymeric materials in various sectors, ranging from packaging to automotive and aerospace industries. [46-48]

A primary application of DSC in the field of polymer science is the determination of glass transition temperatures (T_g). The glass transition temperature of a polymer is a critical parameter that significantly influences the material's mechanical properties, processability, and overall stability. The glass transition is a reversible, second-order phase transition in which a polymer transitions from a rigid, brittle state (glassy) to a flexible, amorphous state (rubbery). By accurately identifying the temperature at which this transition occurs, materials scientists can tailor the properties of the polymer for specific industrial applications. [46-48]

Beyond the determination of the glass transition temperature, DSC is extensively used to examine the crystallization and melting behaviors of polymers. These studies provide a deeper understanding of the semi-crystalline nature of many polymers, their degree of crystallinity, and the structural nuances of their crystal lattices. Through the precise control of crystallization processes, it is possible to engineer polymers with desirable mechanical and thermal properties that are suitable for a wide array of applications. [46-48]

Thermal stability is another crucial aspect of polymer properties that can be evaluated using DSC. Specific applications necessitate the use of polymers that can withstand high temperatures or prolonged exposure to heat without significant degradation of their properties. DSC can be used to identify the onset of thermal degradation and the specific temperatures at which different degradation mechanisms occur. This information is critical when selecting materials for high-temperature applications and for designing polymers with enhanced thermal stability. [46-48]

Furthermore, DSC offers a valuable means of studying the effect of various additives, such as plasticizers or stabilizers, on polymers' thermal and mechanical properties. Additives can profoundly alter the behavior of polymers, leading to changes in their processability, performance, and lifetime. By investigating the interactions between the polymer matrix and the additives, DSC can provide insights into the mechanisms by which these additives affect the properties of the polymer. These insights can guide the development of new materials with improved performance characteristics, ultimately contributing to advancements in various industries. [46-48]

3.3 Structural effect on processing properties

This chapter focuses on investigating the impact of the molecular structure of isotactic polybutene-1 (iPB-1) on its processing properties, with a specific emphasis on phase transitions. Phase transitions, particularly the transformation from phase II to phase I, are of interest due to their implications for industrial applications. Understanding how the structural characteristics of iPB-1 influence these phase transitions is crucial for optimizing processing conditions and ensuring the dimensional stability of manufactured parts.

3.3.1 Time and Industrial Considerations

The phase transition from phase II to phase I in isotactic polybutene-1 occurs gradually over a period of several days. This prolonged transformation time poses practical limitations in industrial settings, where efficiency and productivity are critical. The changing volume and dimensions of the material during the transition necessitate meticulous calculations and measurements, making it more challenging for quality engineers to ensure precise part dimensions.

II. ANALYSIS

4 AIMS AND OBJECTIVES OF THE ANALYSIS

The primary goal of this Master's thesis is to explore the impact of natural aging and direct electrical fields on isotactic polybutene-1 (iPB-1) samples while examining their structure and processing properties. The following specific aims and objectives have been outlined:

1. Prepare isotactic PB-1 samples using two different methods for incorporating additives into the polymer matrix, resulting in samples exhibiting various distribution and dispersion characteristics.
2. Subject the prepared iPB-1 samples to natural aging by positioning them on the faculty building's rooftop, exposing them to a variety of natural forces and effects. Regularly collect and analyze a sample each month to evaluate the influence of natural aging on the polymer's properties.
3. Employ a rheometer to regulate the temperature and apply a direct electrical field to the iPB-1 samples, investigating the effect of this external field on the samples' structural properties and phase transition processes.
4. Investigate the structure of the iPB-1 samples using appropriate analytical methods, such as microscopy and spectroscopy, to determine the impact of varying macromolecular weights, additive mixing techniques, natural aging, and external field exposure on the samples' structural properties.
5. Assess the processing properties of the iPB-1 samples, including crystallization behavior, concerning the structural characteristics and external conditions to which the samples have been subjected.
6. Compare and analyze the results obtained from the various iPB-1 samples and experimental conditions to identify the most effective methods for synthesizing and processing iPB-1 polymers with desired properties and potential industrial applications. By addressing these aims and objectives, this study aims to offer valuable insights into the behavior of isotactic polybutene-1 under different conditions, potentially facilitating the optimization of its processing properties for industrial applications.

5 SAMPLE PREPARATION

5.1 The effect of dispersion and distribution on phase transition II → I

5.1.1 Sample Preparation Method 1: Compression Molding

The initial set of isotactic polybutene-1 (iPB-1) samples was prepared using the compression molding technique. The polymer granules, which consisted of iPB-1 (supplied by LyondellBasell under the commercial name Topyl PB 0110M), were mixed with 0.5 wt.% of additives. The proportions were accurately measured using a laboratory scale. The mixture was then subjected to compression molding in a heated press, set at 160° Celsius for a duration of 5 minutes. Spacers were used during the process to ensure a consistent thickness of 1 mm for each sample. After the molding cycle, the samples were removed from the press and allowed to cool down to room temperature.

5.1.2 Sample Preparation Method 2: Kneading (Extrusion) and Compression Molding

An alternative set of isotactic polybutene-1 (PB-1) samples were prepared by employing a two-step procedure that involved kneading (extrusion) followed by compression molding. Initially, iPB-1 granules (Topyl PB 0110M) were combined with 0.5 wt.% of additives, which were measured using a laboratory scale. The blend was then processed using a kneader (extruder) at a temperature of 190 degrees Celsius and a rotation speed of 100 rpm. Upon obtaining a string-like form from the extruder, it was subjected to compression molding in a heated press at 160° Celsius for 5 minutes, using 1 mm spacers to ensure uniform thickness. The samples were subsequently allowed to cool to room temperature. This method resulted in a different distribution and dispersion of additives within the polymer matrix compared to the compression molding method, thus offering valuable information on the influence of diverse preparation techniques on the samples' properties.

5.2 The effect of natural aging on the phase transition II \rightarrow I

5.2.1 Natural Aging Exposure of iPB-1 Samples

In order to investigate the impact of natural aging on isotactic polybutene-1 (iPB-1) samples, a series of specimens were prepared and exposed to various environmental factors by placing them on the roof of the faculty building. The iPB-1 samples, derived from Toppyl PB 0110M, were prepared using compression molding in a heated press at 160°C for a duration of 5 minutes. For this purpose, 3 mm spacers were employed to form 10x10 cm plates. These plates were then cut into 3x3 cm squares utilizing a hydraulic cutting machine. Each square had a hole drilled into it for attachment to a rope, which was secured on the roof of the building (5th floor), thus exposing the samples to diverse natural forces.



Figure 12 Samples on the roof at the day of the installation



Figure 13 Detailed photo of the samples on the roof, exposed to natural aging

5.2.2 Sample Retrieval and WAXS Analysis Methodology

To assess the effects of natural aging on the polymer's properties, a systematic approach was designed to retrieve and analyze the samples. One sample was retrieved each month, and it was melted at 160°C for a duration of 5 minutes for examination using wide-angle X-ray scattering (WAXS) as the primary analytical tool. The sample was measured immediately after the melting and every 24 hours for five days. This technique allowed for the investigation of structural changes in the polymer matrix resulting from environmental exposure. A total of 160 samples were prepared for the experiment, enabling the study to span over a decade.

5.3 The effect of direct electrical field on phase transition II \rightarrow I

5.3.1 Materials

Isotactic polybutene-1 (iPB-1) samples with two different molecular weights were used in this study. The samples were provided by LyondellBasell and are commercially known as Topyl PB 0110M and Koattro DP 0300M. These materials were selected to investigate the effect of macromolecular chain length on the phase transition under the influence of an external electrical field.

5.3.2 Rheological Measurements

Rheological measurements were performed using an Anton-Paar MCR 502 rheometer equipped with an electrical cell attachment. This allowed for the simultaneous application of a direct electrical field and control of the temperature during the experiments.

5.3.3 Sample Preparation and Experimental Procedure

iPB-1 samples were prepared by placing them in the electrical cell of the rheometer. The temperature was raised from room temperature to 160°C at a linear rate of $\Delta 0.5^\circ/\text{s}$. The influence of the direct electrical field on the samples' structural properties and phase transition processes was investigated by applying three different voltage levels: 0, 3030, and 6060 V/cm. The effect of voltage on the phase transition was studied for both iPB-1 samples with different molecular weights (Topyl PB 0110M and Koattro DP 0300M).

5.3.4 Oscillation Measurements

For the Koattro DP 0300M samples, oscillation measurements were performed to understand further the electrical field's influence on the phase transition. The oscillation measurements were carried out using the same Anton-Paar MCR 502 rheometer and experimental conditions as described in 5.3.3.

6 INSTRUMENTATION AND MEASUREMENT PARAMETERS FOR IPB-1 STRUCTURAL ANALYSIS

In the following subchapter, the instrumentation and measurement parameters utilized for the structural analysis of iPB-1 samples are presented, with a focus on three primary analytical techniques: X-ray diffraction (XRD), differential scanning calorimetry (DSC), and optical microscopy. These techniques were chosen to enable a comprehensive investigation of the phase transitions and structural properties of iPB-1 samples, considering the influences of varying macromolecular weights, additive mixing methods, natural aging, and external field exposure. The subchapter is organized into three sections, each devoted to a specific technique, providing a detailed account of the equipment employed and the measurement values/ranges selected to ensure accurate and reliable results.

6.1 XRD

The samples' percentages of an amorphous phase, phase I, and phase II content were determined using X-ray diffraction (XRD) analysis. Measurements were taken every 24 hours for a period of five days immediately after sample pressing and then again after one month. The XRD measurements were performed using an X'Pert Pro instrument manufactured by Malvern Panalytical Ltd. (United Kingdom). A CuK_α X-ray source with a Ni filter was used, and the Bragg-Brentano configuration was set at 40 kV and 30 mA.

The sample measurements were conducted within the 2θ range of $5\text{-}30^\circ$. This selected range allowed for the detection of peaks corresponding to both phases of iPB-1, as well as peaks of additives reflecting in this spectrum due to their crystalline structure. A representative example of the XRD analysis results is depicted in Figure 14, where peaks corresponding to both iPB-1 phases and a peak corresponding to the α phase of iron oxide can be observed. The XRD data was complemented with Miller indices, which define the atomic planes within the crystal by intersecting them with crystallographic axes.

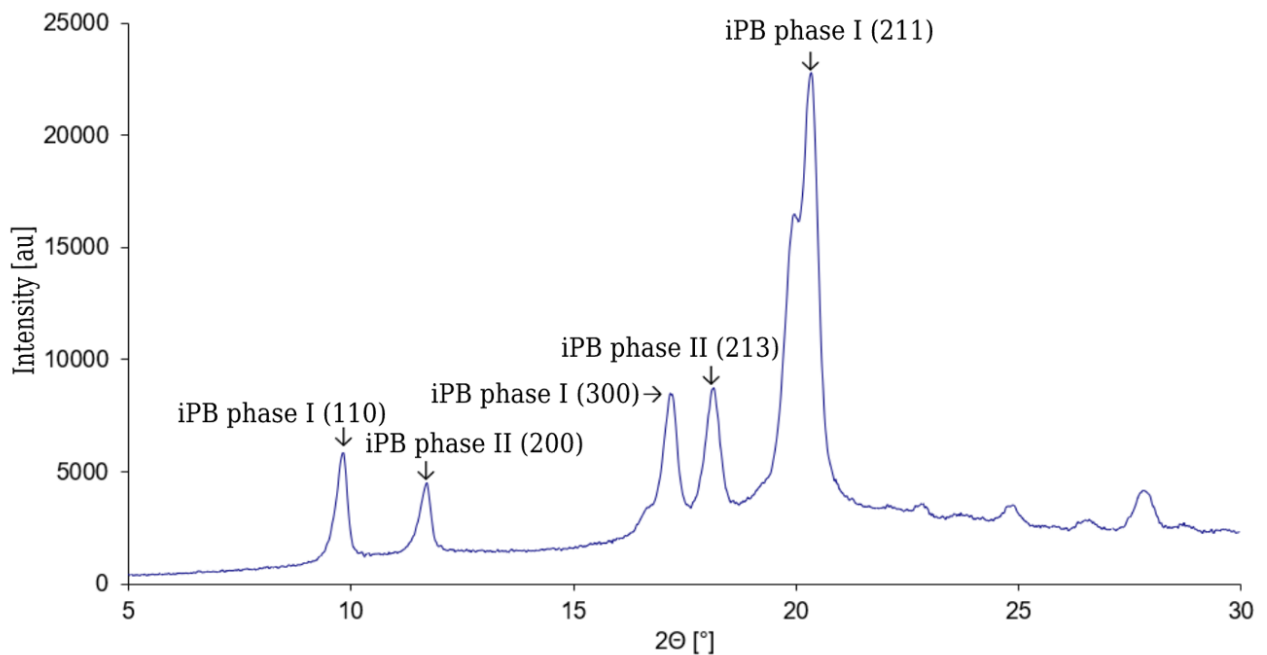


Figure 14 Wide-Angle X-Ray Scattering Pattern of iPB-1 Sample

6.2 DSC

After the crystallization process from the melt, the samples were subjected to DSC analysis using a Mettler Toledo DSC 3 (Switzerland) instrument seven days later. A 5 mg piece was carefully cut from each sample and placed into a 40 μl DSC crucible. The samples were then heated twice, from 60°C to 160°C, at a rate of 10°C/min to determine the melting temperature, T_{M1} and T_{M2} , respectively. Between the heating cycles, a cooling period was observed to determine the crystallization temperature of phase II, denoted as T_c , measured using the same method but in inverse values. The specific enthalpy was calculated by dividing the area under the peak of the curve (which was determined by the STARe Evaluation Software) by the sample weight (weighted by the KERN 770, Germany). Furthermore, the degree of crystallinity was determined by calculating the ratio of the enthalpy to a constant, which indicates the amount of energy stored in the pure crystalline phase (141 J/g for T_{M1} ; 61.5 J/g for both T_c and T_{M2}). These procedures were conducted according to established academic guidelines to ensure the precision and reliability of the research results.

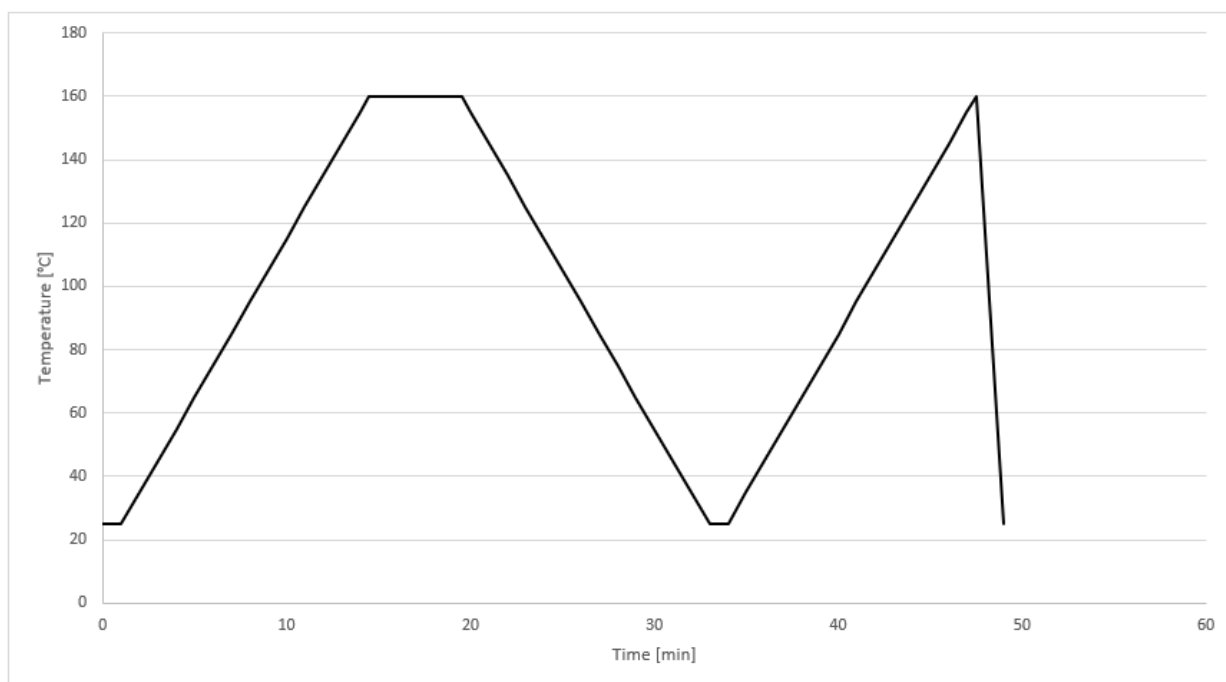


Figure 15 DSC Heating-Cooling Cycle Profile

6.3 Optical microscopy

In order to examine the dispersion and distribution of additives, an optical microscope BX41 (Olympus, Japan) was used to measure each prepared sample. Prior to capturing figures, the sample surface was selectively etched with a solution of 1% KMnO_4 in H_3PO_4 for 30 minutes, which was carried out one day before imaging. Two weeks after melting, the figures were taken to ensure adequate time was given for the sample to reach a stable state. This process was performed in adherence to academic standards to maintain the accuracy and credibility of the research findings.

7 RESULTS AND DISCUSSIONS

This chapter presents the results and discussions surrounding the iPB-1 samples' phase transition from phase II to phase I, focusing on the impact of various factors and conditions on this process. The findings are organized into three main sections, each delving into the effects of a specific aspect on the phase transition.

7.1 The effect of dispersion and distribution on phase transition II → I

This section investigates the influence of dispersion and distribution on the phase transition rate (II→I) in isotactic polybutene-1 (iPB-1) composites containing various additives. The analysis focuses on the results obtained through Wide-angle X-ray Scattering (WAXS) and Differential Scanning Calorimetry (DSC).

Table 1 Data obtained by WAXS

Additive [0.5 wt. %]	Sample preparation	τ [h]	Transformation type	IP [h]	Amorphous phase [% after melting]
-	Heated press	57	N	x	65.6
-	Extruder	65.7	M	22	51.5
*	Heated press	65.2	M	21.8	51.7
CNTs	Extruder	45.1	M	23	47.4
CNTs	Heated press	58.7	M	26	58.4
CFs	Extruder	49.5	M	23	52.2
CFs	Heated press	59	M	23	49.5
Fe	Extruder	46.2	M	22.4	51.1
Fe	Heated press	53	M	27	60.5
Fe ₂ O ₃ (bright)	Extruder	26.4	N	x	44.7
Fe ₂ O ₃ (bright)	Heated press	29.5	N	x	59.5
Fe ₂ O ₃ (dark)	Extruder	59.3	M	22.7	48.8
Fe ₂ O ₃ (dark)	Heated press	61	M	22	51.8
Fe ₃ O ₄	Extruder	44	M	23.9	49.3
Fe ₃ O ₄	Heated press	62	M	23	50.7
MnZn ferrite	Extruder	67.7	M	24	54.2
MnZn ferrite	Heated press	66.5	M	22	51.8
Ruby	Extruder	38	M	22	47.1
Ruby	Heated press	41.7	M	22.5	49.2

WAXS measurements (Table 1) revealed that the majority of samples containing additives prepared on the twin-screw extruder exhibited a shorter phase transformation half-time (τ) compared to those prepared on the press. The only exception was the sample containing the

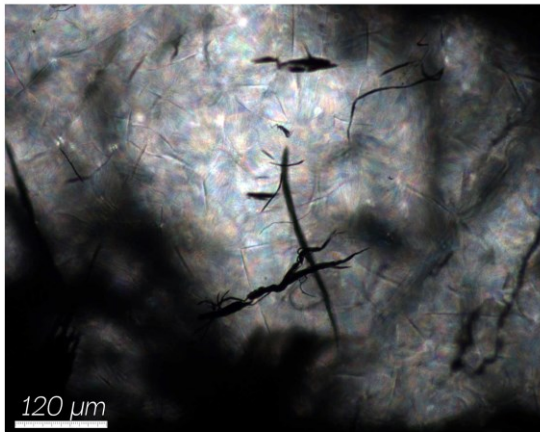
MnZn ferrite admixture. The samples with better dispersion and distribution, such as CNTs, CFs, Fe, and Fe₃O₄, began to behave like nucleating agents (NAs), which was not observed in samples prepared using the press. This finding suggests that improved dispersion and distribution of additives may significantly impact the nucleation efficiency and accelerate the phase transition rate.

Table 2 Data obtained by DSC

Additive [0.5 wt. %]	Sample preparation	TM 1 [°C]	Δ H [J/g]	X [%]	T _c [°C]	Δ H [J/g]	X [%]	TM 2 [°C]	Δ H [J/g]	X [%]
-	Heated press	125.2	61.3	43.5	75.3	35.8	58.2	117.1	36.6	59.5
-	Extruder	126.5	67.8	48.1	74.8	35.5	57.7	117.4	36.6	59.5
*	Heated press	126.6	66.7	47.3	75.4	35.8	58.3	117.6	36.4	59.2
CNTs	Extruder	130.1	72.5	51.4	83.7	38.2	62.2	118.6	39.5	64.2
CNTs	Heated press	127.2	70.9	50.3	79.8	36.7	59.7	118.1	37.7	61.3
CFs	Extruder	126.3	66.3	47.0	81.9	36.2	58.8	117.2	37.0	60.2
CFs	Heated press	128.2	69.7	49.4	76.0	36.6	59.5	117.6	36.7	59.6
Fe	Extruder	128.1	65.0	46.1	73.8	35.2	57.3	117.7	35.1	57.0
Fe	Heated press	127.0	68.1	48.3	80.8	36.7	59.6	117.3	37.0	60.2
Fe ₂ O ₃ (bright)	Extruder	130.0	73.4	52.0	89.8	37.3	60.7	118.0	37.2	60.5
Fe ₂ O ₃ (bright)	Heated press	129.2	73.9	52.4	89.9	38.8	63.1	119.2	40.2	65.3
Fe ₂ O ₃ (dark)	Extruder	128.2	68.4	48.5	81.2	36.6	59.6	118.2	37.1	60.3
Fe ₂ O ₃ (dark)	Heated press	126.5	64.0	45.4	75.8	35.5	57.7	117.9	35.9	58.4
Fe ₃ O ₄	Extruder	128.2	70.0	49.7	77.6	36.9	60	117.1	37.7	61.3
Fe ₃ O ₄	Heated press	128.4	67.0	47.5	76.8	36.0	58.5	117.9	36.2	58.8
MnZn ferrite	Extruder	127.0	66.5	47.1	77.3	36.0	58.5	117.1	37.4	60.9
MnZn ferrite	Heated press	127.2	65.8	46.7	76.0	36.1	58.6	117.6	36.5	59.4
Ruby	Extruder	129	73.5	52.1	83.2	37.9	61.7	117.6	38.3	62.2
Ruby	Heated press	128.9	70.9	50.3	81.3	37.5	61.0	118.3	38.7	63.0

The DSC data (Table 2) provided additional insight into the effect of dispersion and distribution on the thermal properties of the samples. A higher melting temperature (TM 1) was observed primarily for samples prepared on the twin-screw extruder, which indicates enhanced mechanical properties. The only exceptions were samples containing CNTs and Fe₃O₄, where the deviation in values was within the possible measurement uncertainty. It can be inferred that better distribution and dispersion of additives generally lead to the increased melting point, specific enthalpy, and overall crystallinity of the samples.

The optical microscopy images supported the WAXS and DSC findings, showing significant differences in the dispersion and distribution of additives in the samples prepared on the extruder compared to those prepared on the press. The change in dispersion and distribution was especially noticeable in the sample containing CNTs (Figure 16). The sample prepared on the extruder demonstrated considerably better dispersion and distribution than the sample prepared on the press.



Heated press preparation



Extruder preparation

Figure 16 Optical microscopy of samples containing CNTs

7.2 The effect of natural aging on the phase transition II \rightarrow I

The complex domain of phase transitions in materials science has been an area of continuous investigation, with researchers striving to unveil the underlying mechanisms governing these transformations. One area of particular interest is the influence of natural aging on phase transitions, as it can offer crucial information about material stability and the processes that occur over time. In this chapter, the primary focus lies in examining the transition from phase II to phase I, with an emphasis on assessing the role of natural aging.

Regrettably, this study has encountered certain limitations that must be acknowledged. Due to an unfortunate incident involving a broken X-ray diffraction (XRD) machine at the Faculty of Technology, we were unable to obtain a comprehensive set of data for samples aged beyond one and two months. Additionally, we encountered further setbacks when data obtained from a new XRD machine was lost, and despite our best efforts and consultation with technical support, we were unable to recover this information.

Despite these constraints, this chapter aims to present a preliminary analysis of the limited data available for samples aged one and two months. The observed phase transitions will be described and considered in light of the current understanding of the subject, highlighting potential implications and areas for further research. This examination intends to offer an initial perspective on the effect of natural aging on phase transitions, particularly the transition from phase II to phase I, acknowledging the need for additional data and investigation to fully comprehend its significance within the field of materials science.

To evaluate the effect of natural aging on the phase transition II \rightarrow I, the samples were re-melted and subsequently analyzed using Wide-Angle X-ray Scattering (WAXS) for five days. The collected data included the half-time (r) of the phase II-I transition, crystalline content at 2 hours after melting, and crystalline content at 96 hours after melting (Table 3).

Table 3 Phase Transition and Crystallinity of Aged iPB-1 Sample

Aged [months]	r [h]	Crystalline content in 2 hours after melting [%]	Crystalline content in 96 hours after melting [%]
0	50.5	36.88	48.11
1	65.5	37.06	44.29
2	60.5	38.20	50.70

Table 3 presents the half-time (r) of the phase II-I transition and the crystalline content in the samples at 2 hours and 96 hours after melting. From the table, it is evident that the half-time of the phase II-I transition varies with aging time. For the reference sample aged 0 months, the half-time is 50.5 h, while the aged samples at 1 and 2 months exhibit a half-time of 65.5 h and 60.5 h, respectively. This suggests a potential influence of natural aging on the phase transition dynamics (Figure 17).

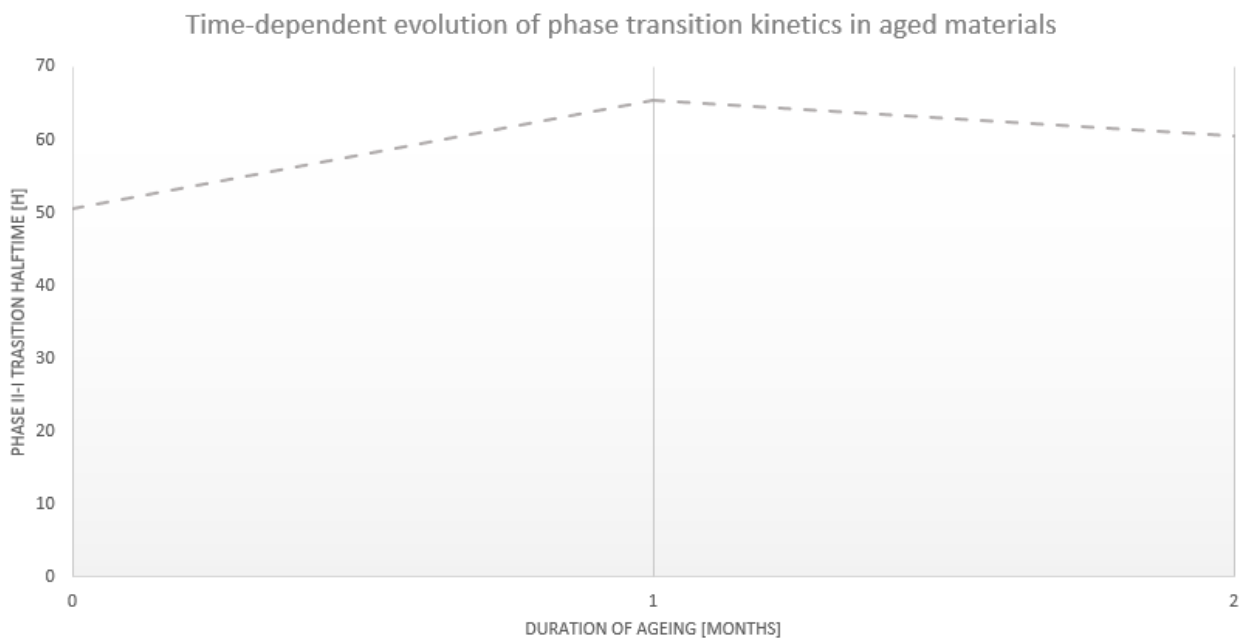


Figure 17 Evolution of phase transition II \rightarrow I half-time for naturally aged iPB-1

An examination of the crystalline content 2 hours after melting (Figure 18) reveals a slight increase with ageing time. The reference sample (0 months) has a crystalline content of 36.88%, while the samples aged 1 and 2 months display crystalline contents of 37.06% and 38.20%, respectively. The observed trend indicates that natural aging may have a minor impact on the initial crystalline content formed in the samples.

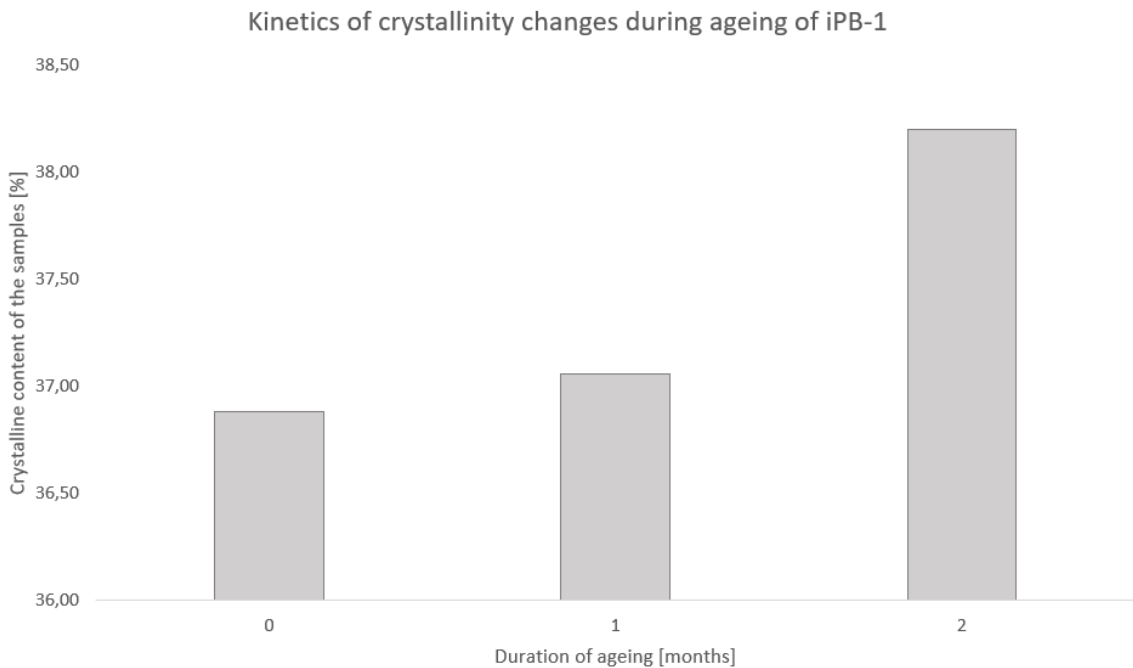


Figure 18 Kinetics of crystallinity changes during ageing of iPB-1 (2 hours after melting)

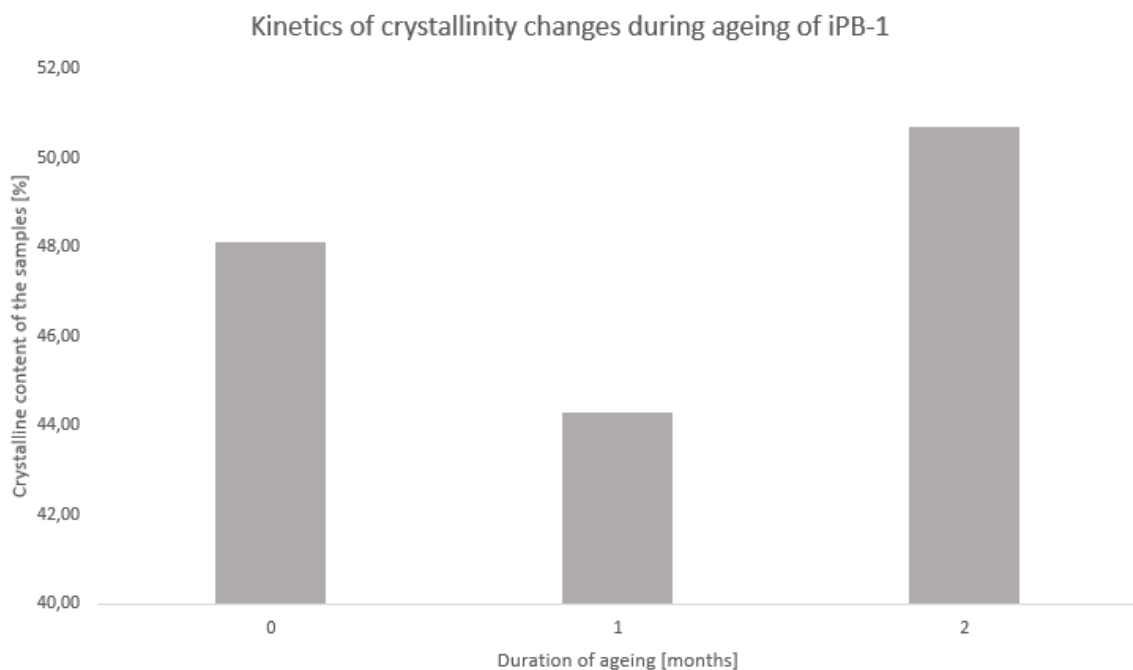


Figure 19 Kinetics of crystallinity changes during ageing of iPB-1 (96 hours after melting)

Furthermore, an analysis of the crystalline content 96 hours after melting (Figure 19) showcases a more complex relationship with aging time. The reference sample (0 months) exhibits a crystalline content of 48.11%. In contrast, the sample aged for 1 month shows a slightly lower crystalline content of 44.29%, while the 2-month-aged sample has a higher content of 50.70%. This non-linear trend implies that the effect of natural aging on the crystalline content at 96 hours after melting is not straightforward and warrants further investigation.

Although the comprehensive dataset could not be obtained due to the issues with the XRD machine, it is important to note that samples aged for half a year (6 months) exhibited distinct visual changes. These samples displayed a yellowish hue and demonstrated a marked decrease in their mechanical properties, as evidenced by the appearance of cracks upon slight bending. These observations suggest the occurrence of material degradation, possibly due to the shortening of macromolecular chains.

The yellowing and brittleness observed in the 6-month-aged samples highlight the potential for significant changes in the material's properties as a result of natural ageing. The observed degradation may impact the material's performance and stability, emphasizing the importance of understanding the influence of natural aging on phase transitions and material properties. Further research, including a more extensive range of aged samples and XRD analysis, is necessary to elucidate the underlying mechanisms and quantify the extent of these changes in materials exposed to natural environmental conditions.

7.3 The effect of direct electrical field on phase transition II \rightarrow I

This chapter aims to investigate the effect of direct electrical field on the phase transition II \rightarrow I in PB using WAXS analysis. Two different macromolecular lengths have been used in order to investigate its effect. For samples, Koattro DP 0300M effect of oscillation has been added as well.

7.3.1 Toppyl PB 0110M samples

Experiments were conducted to investigate the impact of various parameters on the phase II \rightarrow I transition half-time (τ) of samples. The parameters considered include electric field intensity, field application temperature, and whether the electric field was applied during the cooling process. Additionally, a comparison was made between samples prepared using a rheometer and a heated press to determine any influence of the preparation method on the phase transition half-time.

The samples were placed in a rheometer with an electrical cell, melted for 5 minutes, and subjected to electric field application at the specified temperatures. Subsequently, the samples were cooled linearly by the rheometer to 60°C. The electric field applied during the cooling process was either maintained or discontinued, as indicated in Table 4. One sample was prepared using a heated press to evaluate the potential effect of the rheometer on the phase transition half-time.

A notable observation from the results is the significantly longer phase transition half-time of the sample prepared using the heated press (61 hours) compared to all samples prepared in the rheometer. This can be attributed to the fact that the rheometer applied a constant force of 1N (Newton) on the melt, while no force was applied during the heated press process due to the presence of spacers.

The samples subjected to the highest electric field intensity of 6061 V/cm generally exhibit longer half-time values compared to those subjected to lower intensities (3030 V/cm and 0 V/cm). This observation suggests that the electric field intensity indeed impacts the phase transition process; however, higher intensities may not necessarily lead to faster phase transitions as one might initially expect.

Interestingly, the samples subjected to a moderate electric field intensity of 3030 V/cm exhibit slightly faster phase transition half-times compared to those subjected to 0 V/cm, indicating that there might be an optimal electric field intensity that facilitates the phase

transition. This optimal intensity might lie within a range lower than 6061 V/cm, as the half-times at this level seem to be longer than those observed for both lower intensities.

One possible explanation for this phenomenon is that the field could provide sufficient energy to promote the phase transition at moderate electric field intensities, resulting in shorter half-times. However, when the electric field intensity is increased to 6061 V/cm, it might cause additional effects or instabilities in the sample that counteract the facilitation of the phase transition, leading to longer half-times.

Table 4 WAXS Investigation of PB110M: Preparation Parameters, Field Intensity, and Phase Transition Kinetics

Electric Field Intensity [V/cm]	Field Application Temperature [°C]	Field Applied During Cooling [-]	r [h]
6061	160	Not Applied	41.2
6061	160	Applied	38
6061	130	Not Applied	38.7
6061	130	Applied	38
6061	80	Not Applied	42.6
3 030	160	Applied	34.3
3 030	160	Not Applied	38
3 030	130	Applied	39.3
3 030	130	Not Applied	37.7
3 030	80	Not Applied	31.3
0	160	Not Applied	38.5
0	160	Heat Press	61
0	130	Not Applied	40.5
0	80	Not Applied	39.5

Furthermore, it can be observed that the field application during the cooling process also influences the phase transition half-time. In most cases, samples with the electric field applied during cooling exhibited shorter half-times compared to those where the field was not applied during cooling. This indicates that the application of the electric field during the cooling process can potentially accelerate the phase transition.

7.3.2 Koattro DP 0300M samples

The effects of various experimental parameters on the phase II→I transition half-time (τ) of samples were investigated. These parameters include electric field intensity, field application temperature, whether the field was applied during cooling and the presence of oscillation. Additionally, the impact of the sample preparation method, specifically using a heated press versus a rheometer, was also examined.

The results obtained from Table 5 indicate that the phase II→I transition half-time was slightly lower for samples prepared using a rheometer as compared to those prepared using a heated press. One possible explanation for this observation is that the rheometer applied a constant force of 1N on the melt, while the heated press, equipped with spacers, did not apply any force. This difference in force application could have influenced the phase transition process.

Table 5 WAXS Investigation of PB300M: Preparation Parameters, Field Intensity, and Phase Transition Kinetics

Electric Field Intensity [V/cm]	Field Application Temperature [°C]	Field Applied During Cooling [-]	Oscillation [-]	τ [h]
6060	160	Applied	Applied	53.5
6060	160	Applied	Not Applied	52.5
6060	130	Applied	Applied	49
6060	130	Applied	Not Applied	60.3
6060	80	Applied	Not Applied	55
6060	80	Applied	Applied	41
3030	160	Applied	Not Applied	52
3030	160	Applied	Applied	54
3030	130	Applied	Not Applied	52.5
3030	130	Applied	Not Applied	53.5
3030	130	Applied	Applied	51
3030	80	Applied	Not Applied	46
3030	80	Applied	Applied	51.5
0	160	Applied	Not Applied	54
0	160	Applied	Applied	50
0	130	Applied	Not Applied	58.7
0	130	Applied	Applied	50.5
0	80	Applied	Not Applied	42
0	80	Applied	Applied	53
No Cell	80	Not Applied	Not Applied	51
0	160	Heat Press	Not Applied	60

Regarding the electric field intensity, in Table 5, it can be observed that an increase in field intensity from 0 V/cm to 3030 V/cm resulted in a decrease in transition half-time for some samples. However, when the intensity was further increased to 6060 V/cm, the results were inconsistent, suggesting that there might not be a straightforward relationship between electric field intensity and phase II-I transition half-time. It is important to investigate this correlation further to draw concrete conclusions.

The temperature at which the field was applied also seemed to play a role in the transition half-time. In general, as the temperature decreased from 160°C to 80°C, the transition half-time tended to decrease. This suggests that lower temperatures may facilitate the phase II-I transition process.

The application of an electric field during cooling and the presence of oscillation showed mixed results. In some cases, applying the field during cooling and oscillation led to a decrease in transition half-time, while in others, it increased. This indicates that the interaction between these factors and their impact on the phase II-I transition is complex and warrants further investigation.

7.3.3 Conclusion

The results obtained from Table 4 and Table 5 indicate that the phase II-I transition half-time was somewhat lower for samples prepared using a rheometer compared to those prepared using a heated press. This difference, although not as significant for Koattro DP 0300M samples, was more pronounced in the case of Topyl PB 0110M samples. A plausible explanation for this observation is that the rheometer applied a constant force of 1N on the melt, while the heated press, equipped with spacers, did not apply any force. This difference in force application could have influenced the phase transition process, particularly for samples with longer macromolecular chains like Topyl PB 0110M. The constant force of 1N applied to these samples may contribute to increased potential energy, which could lead to a faster half-time of the phase II-I transition.

7.4 Processing properties

In various industries, isotactic polybutene-1 (iPB-1) has been recognized as a material of considerable value, mainly owing to its thermal stability makes it particularly suitable for heat-intensive applications such as hot water pipes. Primarily processed via extrusion, this polymer presents intriguing phase transition characteristics from phase II to phase I, which are of central importance to its processing and applications.

The criticality of extrusion parameters in modulating the phase transition of iPB-1 cannot be overstated. High extrusion pressure, realized through smaller capillaries or increased flow rates, is posited to expedite the phase II-I transition half-time. This hypothesis stems from the comprehension that increased pressure on the melt provides energy transfer to the polymer chains, thereby enhancing the phase transition rate.

Complementing this, the concept of extruding iPB-1 into a pressurized liquid environment, such as oil or water, presents a promising avenue for further exploration. The premise is that such a method could potentially confer additional pressure on the melt, thereby augmenting energy transfer onto the chains and hastening the phase transition half-time.

Discerning additive selection and optimal distribution is paramount in the realm of additive incorporation. The study underscores that a judiciously selected additive, primarily based on its nucleation potential and mechanical enhancement capacity, can not only bolster the mechanical properties of the resultant polymer but also significantly expedite the phase transition.

However, the study also highlights the inherent challenges associated with outdoor applications of iPB-1. Prolonged exposure to environmental elements can instigate natural aging, leading to marked changes in the material's properties. Even with the limited data points available from the natural aging analysis, it is evident that outdoor use can adversely affect the phase transition half-time of iPB-1. This, in turn, could result in dimensional changes over extended periods, which necessitates a cautious approach towards such applications or at least a thorough risk assessment.

CONCLUSION

Investigations into the processing properties of isotactic polybutene-1 (iPB-1) highlights the significant impact of direct electrical fields, dispersion, and distribution of various additives on the phase transition rate (II→I). The primary analysis techniques utilized in these experiments were Wide-Angle X-ray Scattering (WAXS) and Differential Scanning Calorimetry (DSC).

WAXS results indicated an observable correlation between the dispersion and distribution of additives and phase transition rate. Samples prepared on the twin-screw extruder, which demonstrated better dispersion and distribution of additives, generally exhibited shorter phase transition half-times. This suggests enhanced nucleation efficiency, thereby accelerating the phase transition rate. However, this trend was not universally applicable to all additives, as demonstrated by the MnZn ferrite admixture, which deviated from the pattern. This exception underscores the potential influence of the additive's nature on phase transition kinetics.

Furthermore, the influence of natural aging on the phase transition dynamics became evident in the study. The limited data for samples aged one and two months showed that the half-time of the phase II-I transition varied with aging time. This suggests a potential influence of natural aging on the phase transition dynamics, adding another layer of complexity to understanding these processes.

The role of natural aging was further highlighted in the evaluation of crystalline content at different points after melting. A slight increase was observed with aging time in the crystalline content at 2 hours after melting. However, the crystalline content at 96 hours after melting exhibited a more complex relationship with aging time, suggesting that the effect of natural aging on the crystalline content at this time point is not straightforward and warrants further investigation.

Regrettably, the full extent of natural aging on iPB-1 could not be evaluated due to limited data points and technical difficulties with the X-ray diffraction (XRD) machine. However, visual changes and a marked decrease in mechanical properties were observed in samples aged for half a year. These observations suggest the occurrence of material degradation, possibly due to the shortening of macromolecular chains, highlighting the potential for significant changes in the material's properties as a result of natural ageing.

The influence of the electric field and force on the melt during the phase transition process was examined. As observed, the samples prepared using a rheometer, which consistently applied a force of 1N, demonstrated a considerably reduced phase transition half-time compared to the sample prepared using a heated press. This suggests that the application of force on the melt could potentially facilitate the phase transition, speeding up the process.

For the samples with shorter macromolecular weight, such as Koattro DP 0300M, a similar pattern was observed, where the rheometer preparation method, applying a constant force on the melt, resulted in a slightly reduced phase transition half-time. This reaffirms the influence of force application during the melting process on phase transition rates. Notably, as the macromolecular chain length increased, as in the case of Toppyl PB 0110M samples, the force applied on the melt had a more pronounced effect on reducing the phase transition half-time. This may be attributed to the longer macromolecular chains' potential to absorb more potential energy, facilitating a quicker transition from phase II to phase I. This observation underscores the crucial role of molecular characteristics and external forces in governing phase transition kinetics.

It was also noted that the intensity of the electric field has an impact on the phase transition rate. Interestingly, the samples subjected to the highest electric field intensity did not necessarily exhibit the shortest phase transition half-times. Instead, an optimal electric field intensity seemed to exist, beyond which phase transition half-time increased. This complexity may arise from potential instabilities or effects introduced in the sample at higher electric field intensities, leading to a prolonged phase transition process.

Moreover, the application of the electric field during the cooling process appeared to accelerate the phase transition in most instances. This suggests that the presence of the electric field during cooling could enhance the system's energy state, facilitating the transition from phase II to phase I.

The temperature at which the field was applied also emerged as a significant factor. Lower application temperatures generally led to a decreased phase transition half-time, indicating that temperature could play a pivotal role in facilitating phase transitions.

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LIST OF ABBREVIATIONS

WAXS	Wide-Angle X-ray Scattering
DSC	Differential Scanning Calorimetry
iPB-1	isotactic Polybutene-1
r	half-time of phase transition
V	Volt
%(m/m)	percent by mass
XRD	X-ray Diffraction
FTIR	Fourier-Transform Infrared Spectroscopy
N	Newton (unit of force)
°C	degree Celsius (unit of temperature)
h	hours (unit of time)
cm	centimeter (unit of length)

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