FLOW-INDUCED CRYSTALLIZATION OF POLYBUTENE-1 AND EFFECT OF MOLECULAR PARAMETERS

A thesis submitted for the degree of Doctor of Philosophy

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DECLARATION

The author declares that the content of this thesis has not been previously published or written by other authors except where duly acknowledged. The current work has not been submitted previously in whole or in part to qualify for any other academic awards. The thesis is compiled as a result of research carried out since the official commencement of the approved research program.

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NOMENCLATURE

SYMBOLS:

\( a_T \) = shift factor
\( \mathbf{B}_e \) = recoverable strain tensor
\( C_m \) = shape factor
\( C_p \) = molar heat capacity
\( c \) = entanglement density
\( \mathbf{c}^* \) = conformation tensor
\( \mathbf{D} \) = rate of deformation tensor
\( D \) = constraint release parameter
\( De \) = Deborah number
\( De_{crit} \) = critical Deborah number
\( d \) = sample thickness
\( E_a \) = flow activation energy
\( E_D \) = activation energy for the diffusion of elements across the surface between the nano-ordered aggregates and the disordered matrix
\( F_d \) = dependence function of crystallization kinetics on shear rate
\( f \) = factor in molecular stress function (MSF)
\( G \) = growth rate of nucleus or modulus
\( G_0 \) = elastic modulus
\( G' \) = storage modulus
\( G'' \) = loss modulus
\( \Delta G^* \) = free energy barrier
\( \Delta G_f \) or \( \Delta F_f \) = free energy change due to flow
\( \Delta G_q \) = free energy change due to undercooling
\( g \) = relaxation strength
\( H \) = relaxation modulus or spring elastic constant
\( h \) = Planck’s constant
\( \Delta h^o \) or \( \Delta H_f \) = specific heat of fusion
\( \Delta H_K \) or \( \Delta H_0 \) = heat of crystallization
\( \mathbf{I} \) = unit tensor
\( I_c^o \) = equilibrium compliance
\( K \) = crystallization kinetic constant
\( k \) = Boltzmann constant (also \( k_B \)) or thermal conductivity
\( L \) = number of thread-like precursors per unit volume or contour length
\( L_c^* \) = average crystal thickness
\( M \) = torque or molecular weight
\( M_e \) = molecular weight for entanglements
\( M_n \) = number average molecular weight
\( M_{SS} \) = steady-state torque
\( M_{unit} \) = molecular weight of repeat unit
\( M_w \) = weight average molecular weight
\( M_z \) = \( z \)-average molecular weight
\( N \) = number of nuclei per unit volume or Avogadro number
\[ \dot{N} = \text{nucleation rate} \]

\[ N_0 = \text{number of homogeneous nuclei at} \; t = 0 \]

\[ N_f = \text{number of nuclei due to flow} \]

\[ N_{Mu} = \text{mutation number} \]

\[ P = \text{pressure} \]

\[ P_i = \text{initial pressure} \]

\[ P_{SS} = \text{steady-state pressure} \]

\[ p = \text{hydrostatic pressure} \]

\[ Q = \text{heat flow} \]

\[ R = \text{universal gas constant} \]

\[ S = \text{entropy} \]

\[ S = \text{orientational tensor} \]

\[ t = \text{time} \]

\[ t_0 = \text{time zero (when experiment is started)} \]

\[ t_d = \text{delay time} \]

\[ t_{gel} = \text{gelation time} \]

\[ t_{on} \text{ or } t_{onset} = \text{crystallization onset time} \]

\[ t_{on,el} = \text{crystallization onset time in elongation-induced crystallization} \]

\[ t_{on,q} = \text{quiescent crystallization onset time} \]

\[ t_{on,sh} = \text{crystallization onset time in shear-induced crystallization} \]

\[ t_S = \text{shearing time} \]

\[ T = \text{temperature} \]

\[ T_d = \text{disengagement or reptation time} \]

\[ T_g = \text{glass transition temperature} \]

\[ T_k = \text{crystallization point} \]

\[ T_m = \text{nominal melting point} \]

\[ T^o = \text{equilibrium melting point} \]

\[ T_{m1} = \text{first melting point in DSC} \]

\[ T_{m2} = \text{second melting point (reheating run in DSC)} \]

\[ T_{ref.} = \text{reference temperature} \]

\[ \Delta T = \text{degree of undercooling} \]

\[ u = \text{unit orientation vector} \]

\[ U^* = \text{internal energy constant} \]

\[ We = \text{Weissenberg number} \]

**GREEK SYMBOLS:**

\[ \alpha = \text{thermal expansion coefficient or crystallinity} \]

\[ \chi_c = \text{degree of crystallinity} \]

\[ \varepsilon = \text{Hencky strain} \]

\[ \dot{\varepsilon} = \text{strain rate (uniaxial elongation)} \]

\[ \phi = \text{volume fraction of particles} \]

\[ \phi_m = \text{maximum possible volume fraction} \]

\[ \gamma = \text{shear strain} \]

\[ \dot{\gamma} = \text{shear rate} \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{\gamma}_{\text{app}}$</td>
<td>apparent shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}_C$</td>
<td>critical shear rate for granular/oriented boundary layer</td>
</tr>
<tr>
<td>$\eta$</td>
<td>(shear) viscosity</td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>complex viscosity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>zero-shear viscosity</td>
</tr>
<tr>
<td>$\eta_{\text{app}}$</td>
<td>apparent viscosity</td>
</tr>
<tr>
<td>$\eta_E$</td>
<td>elongational viscosity</td>
</tr>
<tr>
<td>$\eta_{\text{SS}}$</td>
<td>steady-state viscosity</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>transpose of velocity gradient</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>characteristic retardation time</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>characteristic time or stretch ratio</td>
</tr>
<tr>
<td>$\lambda_{\text{Mu}}$</td>
<td>mutation time</td>
</tr>
<tr>
<td>$\lambda_{\text{cr,max}}$</td>
<td>crystalline relaxation time</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>dimensionless induction (onset) time</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>specific free energy of nucleus surface or tensile modulus</td>
</tr>
<tr>
<td>$\boldsymbol{\sigma}$</td>
<td>Cauchy stress tensor</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>tensile strength at yield</td>
</tr>
<tr>
<td>$\sigma_{\text{break}}$</td>
<td>tensile strength at break</td>
</tr>
<tr>
<td>$\tau$</td>
<td>relaxation time</td>
</tr>
<tr>
<td>$\tau_{\text{a}}$</td>
<td>stress tensor contribution from amorphous phase</td>
</tr>
<tr>
<td>$\tau_{\text{c}}$</td>
<td>stress tensor contribution from crystalline phase</td>
</tr>
<tr>
<td>$\tau_{\text{max}}$</td>
<td>longest relaxation time</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>reptation time</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency</td>
</tr>
<tr>
<td>$\omega_x$</td>
<td>crossover (between storage and loss moduli) frequency</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>coupling exponent or friction coefficient</td>
</tr>
</tbody>
</table>

**ABBREVIATIONS:**
- **CFS** = Cyclic Frequency Sweep
- **DSC** = Differential Scanning Calorimetry
- **EIC** = Elongation-Induced Crystallization
- **EVF** = Extensional Viscosity Fixture
- **FEM** = Finite Element Methods
- **FIC** = Flow-Induced Crystallization
- **GPC** = Gel Permeation Chromatography
- **HDPE** = High Density Polyethylene
- **LLDPE** = Linear Low Density Polyethylene
- **LMDPE** = Linear Medium Density Polyethylene
- **MPR** = Multi Pass Rheometer
- **MSDS** = Material Safety Data Sheet
- **MSF** = Molecular Stress Function
MWD = Molecular Weight Distribution
SIC = Shear-Induced Crystallization
PE = Polyethylene
PB-1 = Polybutene-1
PP = Polypropylene
i-PP = isotactic Polypropylene
Pl-Pl = plate-plate setup (in rotational rheometer)
PTT = Phan-Thien Tanner (model)
RME = Meissner-type Rheometer
SAOS = Small Amplitude Oscillatory Shear
SAXS = Small Angle X-ray Scattering
TTS = Time-Temperature Superposition
WAXD/S = Wide Angle X-ray Diffraction/Scattering
XPP = Extended Pom-Pom (model)
ABSTRACT

There are two main goals of this thesis: to investigate the flow-induced crystallization behavior of Polybutene-1 (PB-1) samples, and to study the effects of molecular parameters on the crystallization behavior. While flow-induced crystallization is not a new area in polymer research, well-defined experimental methods that allow access to high flow rate range comparable to that encountered in real processing are still lacking. Two types of flow are considered: shear and uniaxial elongational. Regarding the second aim, several molecular parameters considered are: molecular weight, molecular weight distribution, isotacticity, presence of nucleating agents, and copolymer content. For this purpose an array of PB-1 samples were used. It is found that each of these parameters can have significant effect on the crystallization behavior.

Mainly rheological methods were utilized to conduct the flow-induced crystallization experiments. Crystallization onset time is defined from the change in viscosity or other related parameters. The experiments begin with low shear rate range, to ensure that the results are comparable with literature data. In this range we encounter the quasi-quiescent onset time at very small shear rates, which draws an interesting comparison with another physical parameter, the gel time.

Beyond a critical flow rate a decrease in the onset time is seen, and a plateau-and-slope trend is evident for a curve of onset time vs. shear rate. Using a combination of three experimental methods, shear rates ranging from 0.0001 – 500 s$^{-1}$ are successfully achieved, and a good agreement between these methods is observed. Furthermore, a normalization procedure is introduced, which yields temperature-invariant curves for the mentioned range of shear rate.

For the uniaxial elongation flow, the Elongational Viscosity Fixture (EVF) is employed, with the strain rate ranging from 0.0001 – 10 s$^{-1}$. A greater reduction in onset time as compared to shear (at the same shear/strain rate) is observed, and the difference in the onset times for shear and elongation already reaches more than one decade for a flow rate of 10 s$^{-1}$. This quantitative comparison is particularly important, since not so many data on elongation-induced crystallization are available in the literature.

Finally, the thesis compares several flow-induced crystallization models that can be useful as prediction tools and selects one of these models to be compared with the experimental data. A qualitative agreement is found, however for better quantitative prediction the model still needs to be improved.
1. INTRODUCTION

1.1 Background

Polymer crystallization has been an important research area ever since the concept of chain folding was introduced by Storks in 1938 and later validated independently by Keller (1957), Till (1957), and Fisher (1957). In particular, the area of flow-induced crystallization has received a large amount of attention because of its relevance to industrial applications. Almost all polymer processes involve subjecting the polymer to strong flows. The flow situation in real polymer processing is usually complex, involving several types of flow at once. Two of the most important flow types are shear and elongational flows, which will be considered in this project.

In general, the imposition of flow on crystallizing polymers speeds up the crystallization kinetics. However, the influence of flow on crystallization is determined not only by its type and magnitude, but also by the molecular characteristics of the polymer itself. Thus, factors such as molecular weight, breadth of distribution, isotacticity, and presence of additives contribute to the flow-induced crystallization process. It is the aim of physicists and mathematicians to quantify the interrelationship between these various parameters and crystallization kinetics. Clearly, adequate experimental data are essential in developing a crystallization model which can serve as a guide to polymer processing.

1.2 Rationale and Project Goals

The decision to focus on flow-induced crystallization of Polybutene-1 (PB-1 for short) was prompted by several factors. First, there is a considerable industrial interest on this material. Compared to the giants in polyolefins industry, Polypropylene (PP) and Polyethylene (PE), PB-1 is produced in only a small quantity. However, it possesses certain advantages over the other two polyolefins, such as excellent creep resistance at high temperatures, and high flexibility at low temperatures. Thus, the product applications keep expanding and there is a need to know how the molecular parameters should be tailored to give desirable product properties. In turn, the end product properties are influenced considerably by the crystallization process. The second reason is the relatively few literature available on PB-1, compared to PP and PE. Especially, the
elongation-induced crystallization behavior of PB-1 has been scarcely studied. From the experimental point of view, PB-1 is also an easy material to work with, with a moderate crystallization kinetics that would allow an ample time for observation of property change during the process.

The project has two major goals:

1. To study the flow-induced crystallization behavior of PB-1, considering two types of flow: shear and uniaxial elongation.
2. To study the influence of molecular parameters on the flow-induced crystallization. Included are molecular weight, molecular weight distribution, isotacticity, presence of nucleating agents, and copolymer content.

1.3 Structure of the Thesis

The thesis is divided into the following main chapters:

The Literature Review is included in Chapter 2. First, a brief theory on polymer crystallization is presented. Then, the review will move to the significant previous studies of the two important areas in flow-induced crystallization (FIC), composed of shear-induced crystallization (SIC) and elongation-induced crystallization (EIC).

Chapter 3 contains the Experimental part, where the various PB-1 samples used in the study are listed and the methods used for their characterization briefly explained. The chapter also describes the experimental devices employed for the shear- and elongation-induced crystallization study.

In Chapter 4, the experimental work on Quiescent Crystallization is explained. Although it is not the main goal of the thesis, crystallization in quiescent or quasi-quiescent state is important as the basis for analyzing the results in flow-induced crystallization. The difference between the gel point and the crystallization onset time according to the definition given in this thesis is discussed in this chapter.
Shear-Induced Crystallization is the topic of Chapter 5. The chapter covers experimental results in low and high shear rate regions. A typical result of crystallization onset time dependence on temperature is provided for one sample of PB-1, followed by an explanation of the normalization method to construct a temperature-invariant curve. Then, the discussion moves to the results for other PB-1 samples having different molecular parameters (molecular weight distribution, isotacticity, presence of nucleating agents, and copolymer content).

Chapter 6 talks about Elongation-Induced Crystallization. This topic is particularly interesting because not as much literature is available here as for Shear-Induced Crystallization. By utilizing a new experimental device called EVF (Extensional Viscosity Fixture), a large range of strain rates can be applied to the sample. The onset time defined for elongation-induced crystallization is then compared to the one for shear-induced crystallization.

The experimental data collated and discussed in Chapters 5 and 6 are then compared to the model prediction in Chapter 7. A brief review on several existing models for shear- and elongation-induced crystallization is presented, from which a particular model will be selected for comparison with experimental data in this thesis. Along with this, the relevance of the experimental data gained so far to the actual processing conditions will be discussed.

Finally, the most significant findings in this project, as well as suggestions for further research, are listed in Conclusions and Recommendations in Chapter 8.
2. LITERATURE REVIEW

2.1 Crystallization of Semicrystalline Polymers

A crystal is defined as a structure in which the atoms are arranged in a regular, repeated, three-dimensionally periodic pattern (Gedde, 1995). Polymer crystals can be formed in solutions or from the melt, however in the scope of this project only the latter is relevant. Semicrystalline polymers have the ability to crystallize due to their structure regularity. Included in this class are industrial polyolefins like polyethylene, polypropylene, and polybutene-1. Polymers whose chain configuration is bulky or irregular (for example, atactic polymers) tend to form amorphous polymers, which build a glassy structure upon cooling.

The properties of semicrystalline polymer product are therefore dependent on the shape of the crystals formed and on the extent of crystallization. The degree of crystallinity, commonly denoted $\chi_c$, can be determined through well-established experimental methods, for example by dilatometry (Sherwood et al. (1978), Luye et al. (2001), Zuidema et al. (2001)), Differential Scanning Calorimetry (DSC) (Chiu et al. (1993), Schmidtke et al. (1997), Lamberti (2004)), and X-ray scattering (Katayama et al. (1968), Pople et al. (1997), Schmidtke et al. (1997)). Light microscopy is useful to observe the crystal superstructure (e.g. spherulites) (Boutahar et al. (1996), Lee and Kamal (1999), Wassner and Maier (2000)), while the building units of the crystal can be investigated by X-ray scattering or Scanning Electron Microscopy (SEM) (Ulrich and Price (1976), Kim et al. (1997)).

The crystallization process consists of several stages: nucleation, growth, and secondary processes (such as perfectioning and ageing) (Sharples, 1966). In the following subsections, each of these stages is explained briefly.

2.1.1 Nucleation

The nucleation stage is the most important and yet the least understood process in polymer crystallization. Numerous factors affect the process, for example time, temperature, impurities, nucleating agents, and presence of flow. According to Gedde (1995), there are two main types of nucleation: athermal and thermal. Athermal or instantaneous nucleation refers to the case where critical nuclei are formed at time $t =$
0 and grow with a uniform growth rate, and therefore it is simple to simulate. In thermal nucleation, growing entities are formed at a constant rate in space and time, indicating a sporadic mechanism. Nucleation process can also be classified into either homogeneous (from pure melt or solution) or heterogeneous (induced by impurities or nucleating agents). Since commercial polymers normally contain residual catalysts and additives, heterogeneous nucleation is more common, and the process occurs athermally.

There have been several theories on how nucleation proceeds at the molecular level. Hess and Kiessig (1944) first introduced the fringed-micelle model, where there are alternating ordered and amorphous regions, with each polymer chain taking part in several regions. However, this picture was considered to be too simple for many cases. For single crystals formed in solution, it was confirmed by Keller (1957) that the polymer chains form tight and regular folds perpendicular to the growth direction. This observation gave birth to the chain-folded model, and the conceptual difference to the fringed-micelle model can be seen in Figure 2.1. Flory (1962) proposed a modified version called the random-switchboard model, which is a combination of the fringed-micelle and the lamellae models. Here, one long chain may statistically participate in several rows of folds (lamellae) instead of just forming one long row (lamella) by tightly folding on itself.

Figure 2.1. Morphological models of crystallized polymers: (a) fringed-micelle model (Hess and Kiessig, 1944), and (b) chain-folded model (Keller, 1957).
In polymer melts, the situation is more complicated because there are entanglements between chains and there is a strong competition with other chains for the folding process. However, similar to solution-grown crystals, Transmission Electron Micrograph (TEM) photos prove that melt-grown crystals are composed of stacked lamellae, with each lamella containing the folded parts of polymer chains and the amorphous region consisting of the unfolded parts (Gedde, 1995).

The formation of a stable nucleus involves an arrangement of polymer chains by reptation and/or rotation to form bundles (clusters) having a favourable position and orientation. When the bundle reaches a critical size, \( r^* \), the nucleus becomes stable and growth is kinetically favoured. The free energy barrier, \( \Delta G^* \), that has to be overcome for the stable nucleus is calculated as follows (Gedde, 1995):

\[
\Delta G^* = \frac{16\pi\sigma^3 (T_m^o)^2}{3(\Delta h^o)^2 \Delta T^2}, \quad \text{where}
\]

\( \sigma \) = specific free energy of nucleus surface (J/m\(^2\)),

\( T_m^o \) = equilibrium melting point (K),

\( \Delta h^o \) = specific heat of fusion (J/m\(^3\)), and

\( \Delta T \) = degree of undercooling (K).

Turnbull and Fisher (1949) formulated the nucleation rate as a function of temperature as:

\[
\dot{N} = N_0 e^{-\left(\frac{E_D}{kT} \frac{\Delta G^*}{kT}\right)}, \quad \text{where}
\]

\( N_0 \) = number of homogeneous nuclei at \( t = 0 \) (m\(^{-3}\)),

\( E_D \) = activation energy for the diffusion of elements across the surface between the nano-ordered aggregates and the disordered matrix (J/mol), and

\( k \) = Boltzmann constant.

By combining the dependence of critical nucleus size and polymer chain mobility with temperature, it is shown that a graph of nucleation rate vs. temperature has a bell shape (Figure 2.2), with a zero rate at equilibrium melting temperature and glass temperature, and a maximum rate in the middle.
2.1.2 Growth

The most widely used treatment on crystal growth was proposed by Lauritzen and Hoffmann (1973, 1976). In their theory, an energetic free energy barrier controls the average crystal thickness ($L_c^*$), which in turn controls the growth rate. It is also assumed that the growth rate, $G$, varies linearly with time and is a function of the degree of undercooling, which is in accord with most experimental observations.

After the stable nucleus has been formed (primary nucleation), crystallization progresses with the diffusion and attachment of chain segments in the undercooled melt onto the substrate having a width $L$ (secondary nucleation). The chains then arrange themselves into the appropriate crystallographic register. The description of how a polymer segment attaches to the substrate and fold is given in Figure 2.3.

![Figure 2.2. Nucleation rate as a function of temperature.](image1)

![Figure 2.3. Formation of crystal lamella by attachment and folding of polymer segment.](image2)

(a = stem width, $b$ = stem thickness, $g$ = direction of stem buildup).
The Lauritzen-Hoffman (LH) theory, classifies the growth process into three regimes, the characteristics of which are given in Table 2.1 (Gedde, 1995).

### Table 2.1. Description of growth rate regimes in the LH theory.

<table>
<thead>
<tr>
<th>Regime</th>
<th>Characteristics</th>
<th>Growth Rate Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$g &gt; i$, lateral stem growth rate ($g$) is large compared to rate of secondary nuclei formation ($i$) – stems cover the entire length of substrate.</td>
<td>$G_I = G_{0I} \exp \left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp \left(-\frac{4b\sigma_L}{\Delta g T_c}\right)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{0I} = \frac{kT_c}{h} J_1 \exp \left(\frac{2ab\sigma_L}{kT_c}\right)$</td>
</tr>
<tr>
<td>II</td>
<td>$g &lt; i$, stacks of nuclei formed before the lateral growth of the stems completely covers the substrate.</td>
<td>$G_{II} = G_{0II} \exp \left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp \left(-\frac{2b\sigma_L}{\Delta g T_c}\right)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{0II} = \frac{kT_c}{h} \exp \left(\frac{(2\psi - 1)ab\sigma_L}{kT_c}\right)$</td>
</tr>
<tr>
<td>III</td>
<td>$g &lt;&lt; i$, very fast formation of nuclei stacks, heavily patchy covering of substrate length.</td>
<td>$G_{III} = G_{0III} \exp \left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp \left(-\frac{4b\sigma_L}{\Delta g T_c}\right)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{0III} = \frac{kT_c}{h}$</td>
</tr>
</tbody>
</table>

Although the LH theory is still the most widely used concept to assess crystallization processes, the original model has received criticisms over the years and several versions have been introduced, the most recent of which was given by Hoffmann and Miller (1997). This version incorporates the reptation theory (de Gennes, 1966) to calculate the rate of deposit of stem onto substrate, hence it improves the application of LH theory for heavily entangled melts.

One of the important oppositions to LH theory is the Sadler-Gilmer theory (1984), which proposes that the free energy barrier to nucleation has an entropic, rather than enthalpic, origin. Therefore, through attachment and detachment processes, the nucleating stem finds the satisfactory conformation to start growing on the substrate. Both the LH and Sadler-Gilmer theories are grouped under the heading of kinetic growth theory. The equilibrium theory, on the other hand, states that growth is not
controlled by kinetic factors but decided by the minimum free energy. An example was proposed by Peterlin et al. (1962). However, experimental data and simpler analysis support the popularity of kinetic theories, and equilibrium theories are rarely discussed nowadays.

2.1.3 Recent Conceptual Models on Crystallization

Recent experimental observations have sparked several suggestions on crystallization pathway that differ from the “conventional wisdom”, i.e., the LH theory. For example, Strobl (2000) proposed that an intermediate state may precede the formation of lamellar crystallites from the amorphous, entangled melt. This intermediate state is in the form of a mesomorphic layer, composed of stretched chain sequences in a liquid-like cylinder packing, which then thickens into a “granular crystal layer”, set up of crystal blocks in a planar assembly. It is the merging of these granular layers that finally form the lamellar structure. The schematic of the process is given in Figure 2.4. Small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM) pictures on polyethylene and syndiotactic and isotactic polypropylenes give evidence of the existence of a mesomorphic state.

![Figure 2.4. Schematic of nucleation progress via mesomorphic and granular layers according to Strobl (2000).](image)

Another concept based on SAXS and WAXS studies was forwarded by Terrill et al. (1998). According to this group, nucleation begins by spinodal decomposition process, rather similar to liquid-liquid phase separation observed for polymer blends. This process is triggered by one region in the polymer having chain segments that are
appropriate for crystallization and another region that does not have them, which eventually becomes the amorphous part. The different energy densities owned by each region will act as the driving force for the phase separation.

These novel concepts are still debatable and they have received several criticisms. Lotz (2000), for example, claimed that in crystallization of an isotactic polypropylene, the process is likely to be highly substrate-determined. Because the depositing stem forms a helical geometry and faces rather high constraints of crystal symmetry, Strobl’s suggestion that molecules form pseudo-crystalline bundles with random arrangements does not seem to be valid in this case. Janeschitz-Kriegl (2003) questioned the possibility of spinodal decomposition based on the experimental evidence that the number of participating molecules in the formation of athermal nuclei is very low, compared to the total number of molecules per unit volume. The formation of random, widely-separated spots in a sea of amorphous matter is difficult to be reconciled with a picture of nucleation process as a neat, liquid-liquid phase separation. In summary, although the recent theories present interesting alternative views on nucleation, their widespread application is still unlikely. The main issue in such experiments is the limitation of methods that are sensitive enough to probe very early stages of crystallization. On the other hand, without a careful comparison of several methods, it is difficult to interpret the data objectively.

2.1.4 Overall Kinetics of Primary Crystallization
Avrami (1939, 1940, 1941), Evans (1945), and Kolmogoroff (1937) in the 1930s to 1950s independently proposed equations describing the kinetics of phase change in crystallization. The Avrami equation (or often generalized to Kolmogoroff-Avrami-Evans (KAE) approach) is still widely popular because of its simplicity, although it is limited to describing the empirical, macroscopic results without giving insights on how nucleation and growth actually proceed on molecular scale (Wunderlich, 1973). With this approach, the degree of crystallization ($\chi$) can be calculated as follows:

$$\chi(t) = 1 - \exp(-E(t)) \quad (2.3)$$

$$E(t) = C_1 \int_0^t \hat{N}_t(s) \left( \int_s^t G(z) dz \right) ds + C_2 N_{at} \left( \int_0^t G ds \right)^n, \text{ where} \quad (2.4)$$
\( E(t) \) = total volume of the growing nuclei, neglecting impingement effects,

\( C1, C2 \) = geometry constants,

\( \dot{N}_t \) = rate of formation of thermal (or homogeneous) nuclei,

\( N_{at} \) = number of athermal (or heterogeneous) nucleation sites,

\( G \) = growth rate of nuclei, and

\( n \) = number of orthogonal crystal growth directions.

It is important to note that \( \chi = 100\% \) refers to the maximum crystallinity of the sample that can be obtained, but it does not necessarily mean that there is no amorphous phase present in the sample.

By assuming an isothermal crystallization, the time dependence of nucleation and growth is eliminated, and the equation reduces to:

\[
E(t) = K_1 t^{n+1} + K_2 t^n \approx Kt^m
\]  \hspace{1cm} (2.5)

\[
\chi(t) = 1 - \exp(-Kt^m)
\]  \hspace{1cm} (2.6)

The parameter \( K \) is called the Avrami constant (\( K_1 \) refers to the dimensionality of the crystal shape, and \( K_2 \) indicates instantaneous (\( K_2 = 0 \)) or sporadic (\( K_2 = 1 \)) nucleation), and \( m \) the Avrami index. The value of \( m \) indicates whether the nucleation is heterogenous or homogeneous, and which shape of crystal superstructure is expected, as listed in Table 2.2.

<table>
<thead>
<tr>
<th>( m = K_1 + K_2 )</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>Crystallization characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3</td>
<td>1</td>
<td>Spherulitic growth, homogeneous nucleation</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
<td>Spherulitic growth, heterogeneous nucleation</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>Disc-like growth, homogeneous nucleation</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>Disc-like growth, heterogeneous nucleation</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>Rod-like growth, homogeneous nucleation</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>Rod-like growth, heterogeneous nucleation</td>
</tr>
</tbody>
</table>

Often, the Avrami exponent found by fitting experimental data gives fractional values, which suggests that there is a mix between several growth types and/or nucleation mechanisms (Mandelkern (1964), Sharples (1966)). Although the Avrami equation is practical in describing the overall crystallization process, its application is
confined to the isothermal case. Therefore, several modifications based on the Avrami equation have been introduced to calculate the crystallization rate in non-isothermal conditions. Several examples of these are the Ozawa model (1971), the Nakamura isokinetic model (1972, 1973), and the Kamal model (1983). Schneider et al. (1988) also introduced a derivative version of the crystallization rate equation, which is simpler to use.

Either for isothermal or non-isothermal case, the crystallization kinetic curve derived from any of the models generally shows agreement with experimental data only up to a certain crystallization degree ($\chi < 0.7$ or $0.8$) (Chan et al., 1995). This part corresponds to the primary crystallization, i.e. nucleation and growth. Beyond this point, a marked decrease in crystallization rate is often observed due to cessation of primary crystallization and dominance of secondary crystallization.

2.1.5 Secondary Crystallization

Secondary crystallization becomes significant at later stages of crystallization (for example, after the impingement of spherulites), although it is still debatable when primary crystallization ceases and secondary crystallization begins. The process can take place in many forms, for example lamellar thickening (Marand and Huang, 2004), refinement of existing crystals (Schultz et al., 1980), or formation of secondary lamellar stacks from remaining amorphous regions between the spherulites (Verma et al., 1996).

The Avrami equation is also used to investigate the kinetics of secondary crystallization, although in a modified form, since the original version can account only for early stages of crystallization (Perez-Cardenas et al., 1991). Lu and Hay (2001) reported that primary and secondary crystallization processes occur consecutively, indicated by a sharp change in the Avrami exponent from 2.6 to 1.2 (in PET). As indicated by the Avrami exponent, the primary crystallization has a three-dimensional growth (spherulitic) whereas the secondary process is more one-dimensional (fibrillar). Such difference was also observed for nylon 12,12 (Ren et al., 2004). On the other hand, Kolb et al. (2001) concluded that for isotactic polypropylene (iPP), both processes occur simultaneously and secondary
crystallization is strongest at the boundary of the spherulite, independent of the growth state of the spherulite.

In several polymorphic (having more than one crystal form) polymers, secondary crystallization also influences the proportion of the crystal forms. This is in turn has a direct effect on the end properties, such as optical transparency and mechanical properties. For example, in PP, the $\gamma$ phase (as opposed to $\alpha$ and $\beta$ crystals) forms predominantly during secondary crystallization, which can be attributed to the low-molecular-weight portion fractionated as the amorphous region in primary crystallization. In the case of PB-1, the transformation from the metastable Form II (tetragonal unit crystal, formed directly from undercooled melt) to Form I (hexagonal unit crystal, formed during the aging process) continues long after primary crystallization has been completed (see Section 3.1.1.2 for more details on polymorphism).

2.2 Flow-Induced Crystallization
Virtually all types of polymer processing involve flow- or deformation-induced crystallization, which renders it one of the most widely and continuously studied areas in polymer science. Up until the 1970s, however, the majority of studies on crystallization had been focusing on quiescent crystallization or flow-induced crystallization for polymers in solution, in which the situation is simpler than in polymer melts because of the much smaller population of polymer chains per unit volume. While there was clear evidence (Haas and Maxwell, 1969) showing that in flow-induced crystallization of polymer melts, the crystallization kinetics are significantly enhanced compared to that in quiescent condition (often to the extent of several magnitudes), a systematic approach to the phenomenon had not been substantial. As scientists realized its immediate relevance to the rate of production and end-product properties, the flow of research activities began. Two major types of flow are present in polymer processing: shear and elongation. In the following subchapter, some of the important studies on shear- and elongation-induced crystallization are reviewed.
2.2.1 Shear Flow

2.2.1.1 Early Research

Several important findings were produced in the period of 1970-1980 that laid the ground for further initiatives. Lagasse and Maxwell (1976) used a parallel plate sliding rheometer to investigate the shear-induced crystallization (SIC) of polyethylene (PE), with a shear rate range of 0.03 – 30 s\(^{-1}\). A crystallization induction or onset time was introduced but not clearly defined. It was found that there exists a critical shear rate, below which the shear flow has a negligible effect on the induction time. Therefore, the plateau-and-slope curves seen in Figure 2.5 are typical for SIC results. Furthermore, at the induction time, the total strain was observed to approach a constant value at high shear rates (the slope approaches –1). This prompted the discussion whether SIC is a shear rate- or strain-controlled process.

![Figure 2.5. Reduction of crystallization induction time above a critical shear rate, for a sample of polyethylene (Lagasse and Maxwell, 1976).](image)

A similar device was also used by Wereta and Gogos (1971), although with a slightly different arrangement that caused the thickness of the sample to decrease during shearing. In this case, step-shear was applied to undercooled polybutene-1 (PB-1) melt. Their study confirmed that PB-1 sample crystallizing under shear gives a mixture of Form I and Form II crystals, as opposed to exclusively Form II crystals when a melt is cooled under quiescent condition.

Other experimental methods, such as that using coaxial cylinder rheometer (Kobayashi and Nagasawa, 1970), biconical rheometer (Tan and Gogos, 1976), and
rotary parallel-plate (Wolkowicz, 1978), were used. Wolkowicz (1978) concluded that the main contribution of shear in crystallization process is enhancing the nucleation step, while the growth rate is similar to that in quiescent condition. Experimental data from Tan and Gogos (1976) show that even at temperatures above the melting point, SIC still occurs as long as the shear is strong enough.

The morphology of crystals formed under shear was studied, for example, by Haas and Maxwell (1969). They imposed a creep flow (i.e. objecting the sample to a constant stress) on linear PE and PB-1 samples. It was observed that stress caused a large multiplication of nuclei formed, and even led to formation of oriented morphologies (the so-called “shish-kebab” or “row-structures”).

2.2.1.2 Recent Developments
Since the 1990s, the research activities on flow-induced crystallization in general and SIC in particular have picked up pace, along with the growing availability of commercial rheometers. Indeed, several commercial devices arose from initial investigations on SIC, for example the Multi Pass Rheometer or MPR (Mackley et al., 1995, 2000) and the Linkam Shear Cell (Mackley et al., 1999), both developed at Cambridge University. Table 2.3 lists several experimental devices that have been used to study SIC in the last 15 years.

Table 2.3. List of experimental methods used in SIC study since the 1990s. (BR = birefringence, CS = continuous shear, LI = light intensity/turbidity, LM = light microscopy, SAOS = small amplitude oscillatory shear, SALS = small angle light scattering, SAXS = small angle X-ray scattering, TEM = transmission electron microscopy, WAXS = wide angle X-ray scattering. iPP = isotactic polypropylene, PCL = poly(ε-caprolactone), HDPE = high density polyethylene, LMDPE = linear medium density polyethylene).

<table>
<thead>
<tr>
<th>Reference</th>
<th>Experimental Device (Method)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devaux et al. (2004)</td>
<td>Linkam cell, sliding plate hot stage (LI, LM, SALS)</td>
<td>iPP</td>
</tr>
<tr>
<td>Acierno et al. (2003)</td>
<td>plate-plate rheometer, Linkam cell (CS, LI)</td>
<td>PB-1</td>
</tr>
<tr>
<td>Watanabe et al. (2003)</td>
<td>coaxial cylinder apparatus (LM)</td>
<td>PB-1</td>
</tr>
<tr>
<td>Bove and Nobile (2002)</td>
<td>cone-plate rheometer (SAOS)</td>
<td>PB-1</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Method/Instrumentation</td>
<td>Polymer</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>-----------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Kumaraswamy et al. (1999, 2000, 2002)</td>
<td>slit flow cell (WAXS, LI, BR, TEM)</td>
<td>iPP</td>
</tr>
<tr>
<td>Masubuchi et al. (2001)</td>
<td>SFTR (SAOS)</td>
<td>iPP</td>
</tr>
<tr>
<td>Pogodina et al. (2001)</td>
<td>rheo-optical device (SALS)</td>
<td>iPP</td>
</tr>
<tr>
<td>Floudas et al. (2000)</td>
<td>plate-plate rheometer (LI, BR)</td>
<td>PCL</td>
</tr>
<tr>
<td>Mackley et al. (2000)</td>
<td>MPR (BR, WAXS)</td>
<td>HDPE</td>
</tr>
<tr>
<td>Somani et al. (2000)</td>
<td>Linkam cell (SAXS, TEM)</td>
<td>iPP</td>
</tr>
<tr>
<td>Wassner and Maier (2000)</td>
<td>plate-plate rheometer (CS)</td>
<td>iPP</td>
</tr>
<tr>
<td>Duplay et al. (1999)</td>
<td>fiber pull-out (LM)</td>
<td>iPP</td>
</tr>
<tr>
<td>Vleeshouwers and Meijer (1996)</td>
<td>cone-plate rheometer (SAOS)</td>
<td>iPP</td>
</tr>
<tr>
<td>Liedauer et al. (1993, 1995)</td>
<td>Slit flow cell</td>
<td>iPP</td>
</tr>
<tr>
<td>Monasse (1995)</td>
<td>Sliding plate hot stage (LM)</td>
<td>LMDPE</td>
</tr>
</tbody>
</table>

Naturally, each of the methods listed above has its own advantages and limitations. There is often a debate among researchers whether it is more instructive to impose a step shear or continuous shear. Actually, they are both important for different processing stages or types. For example, in injection molding the melt is subjected to a strong shear for a short time. On the other hand, in extrusions the material experiences continuous shear. Another factor that complicates real processing conditions is non-isothermal crystallization, in which the analysis can be very difficult. Therefore, most of the crystallization experiments are conducted isothermally.

Cone-plate and plate-plate rheometers are relatively simple to use and they can also be put into both step and continuous shearing modes, hence they are often used for SIC studies, as seen in Table 2.3. The disadvantage of this method is the practical upper limit of shear rate, which is usually still below $10 \text{ s}^{-1}$. From the theoretical point of view, the cone-plate setup is preferred over plate-plate because the dependence of shear rate on radius is eliminated. However, the cone-plate setup requires the sample to have an exact thickness, hence one has to be careful when using it for experiments involving temperature changes.
In the experiments of Vleeshouwers and Meijer (1996), the sample was sheared \((0 < \dot{\gamma} < 10 \text{ s}^{-1})\) for a certain time \((0 < t < 200 \text{ s})\) at the annealing temperature and then quenched to the crystallization temperature. It was found that shear history enhances crystallization in much the same way as if the shear was directly applied to an undercooled sample. Furthermore, the shearing rate and time affect the result differently; short time shearing at high rate was found to be the most effective. The influence of molecular parameters is unclear, since some of the high molar mass tail might have experienced degradation during shear at the annealing temperature.

Bove and Nobile (2002) observed that both a critical shear rate and a critical shear strain are required for the flow to effectively enhance the crystallization kinetics. By monitoring the evolution of the storage modulus \(G'\) during crystallization, they defined an overall crystallization constant \(k\). The flow sensitivity parameter is then introduced as the ratio of \(k\) values in shear-induced and quiescent states (at the same temperature). A comparison of two PB-1 samples having different molecular weights shows that the sample with higher molecular weight is more sensitive to flow. In quiescent state, however, the molecular weight has no effect on the rate of crystallization. A relatively low shear rate range \((0.01 – 1 \text{ s}^{-1})\) was applied.

Similar conclusions were drawn by Acierno et al. (2003) regarding the effect of molecular weight on quiescent and shear-induced crystallization, also on samples of PB-1. Continuous shear ranging from \(10^{-3}-10 \text{ s}^{-1}\) was used, and the crystallization onset time was determined from turbidity measurements. A scaling law, which combines the effects of molecular weight and shear rate on SIC, was proposed by defining the Weissenberg number \(We\) and the normalized onset time \(\Theta\):

\[
We = \dot{\gamma} \cdot \tau_{\text{max}},
\]

\[
\Theta (T) = \frac{t_{\text{on}}(\dot{\gamma})}{t_{\text{on,q}}},
\]

where \(\tau_{\text{max}}\) is the longest relaxation time of the sample, a parameter that strongly depends on molecular weight.

When a plot of \(\Theta\) vs. \(We\) is made, the data points from samples having different molecular weights (but similar molecular weight distributions) fall into one plateau-
and-slope curve. Furthermore, from microscopy observations, they found a critical \( We \approx 150 \) where the transition from spherulitic into rod-like crystals occurs.

![Figure 2.6](image.png)

**Figure 2.6.** A plot of normalized crystallization onset time as a function of the Weissenberg number at 103 °C, for four PB-1 samples with different molecular weights (Acierno et al., 2003).

Contrary to the two studies above, Wassner and Maier (2000) found that for their iPP samples, the high molecular weight sample crystallizes slower in quiescent condition. The possible explanation for this is that the long molecules take longer to organize themselves when no orienting flow is present. The highest shear rate attempted here was just 0.16 s\(^{-1}\), but even this was already enough to reduce the onset time by one decade compared to that in the quiescent state.

Devaux et al. (2004) added one more criterion to the shearing experiment: in step shear experiments, the instant when shear is started was varied, for a given shear rate and time. Interestingly, as long as this starting time is earlier than the moment when viscosity starts to increase, no effect on crystallization kinetics was observed. This indicated that the mechanism of crystallization is the same for quiescent and shear-induced conditions.

The fibre pull-out method introduced by Monasse (1992) and then used by Duplay et al. (1995) to study a wide array of iPP samples can generate shear rates up to 400 s\(^{-1}\). However, the amount of total strain is limited to the length of the fibre. Contrary to what was suggested by Wolkowicz (1978), they found that shear also increases the
growth rate of nuclei, in addition to the enhancement of nucleation rate, whereby both contribute to the overall crystallization kinetics.

The MPR device developed by Mackley et al. (2000) is the only device so far that can impose industrial range shear rates, up to around 2000 s\(^{-1}\). Typically, shear rates used for injection molding processes range between \(10^2 \text{ – } 10^4\) s\(^{-1}\) (Koppelmann, 1987; Isayev, 1995). The experiment involves forcing the sample through a rectangular slit with a width of 1 mm, therefore creating a shear flow. Rheo-optics and rheo-X-ray results on an HDPE sample show that strong shear can also induce the molecular “coil-stretch” transition and result in fibrous crystal structures, which are normally associated with extensional flows. Interestingly, if the apparent wall shear rate was increased from 225 s\(^{-1}\) to 2250 s\(^{-1}\), the fibrous structures did not appear, probably due to the wall slip phenomenon.

Birefringence and light/X-ray scattering methods are useful to detect density and orientation fluctuations in the sample, therefore they are more sensitive for early stages of crystallization. Devaux et al. (2004) and Pogodina et al. (2001) observed that density fluctuations precede orientation fluctuations under both quiescent and shear-induced conditions, but with a shift in the time scale for the maxima. The density fluctuations can be attributed to formation of local dense zones in the sample that could act as nuclei precursors, while the change in molecular conformations in the system causes the orientation fluctuations.

Figure 2.7. Schematic of the fibre pull-out device. \(V_f\) = fibre displacement speed (Jay et al., 1999).
A schematic representation of nucleation and growth is proposed by Somani et al. (2000) based on SAXS results on iPP samples subjected to a step shear (Figure 2.8). The flow created clusters of aligned chain segments. These segments induce primary nuclei to form in the flow direction, from which crystal lamellae grow perpendicular to the flow direction. Although the shear rates were rather high (up to $10^2 \text{ s}^{-1}$), no evidence of extended chain structures were observed, probably because of the limit in strain or the molecular weight of the sample. In fact, the researchers suggested that for a certain shear rate (or strain), only chains having molecular weights greater than a critical value will become oriented, while the shorter chains relax back into the coiled state after flow is stopped.

![Schematic representation of nucleation and growth](image)

**Figure 2.8.** Crystallization process from (a) sheared melt to (b) formation of primary nuclei and lamellae growing perpendicularly from them (Somani et al., 2000).

### 2.2.1.3 Research by Linz Group

The continuous research on flow-induced crystallization by the group at Linz University in Austria for more than 20 years has contributed significantly to the concept and understanding of the crystallization process. To investigate shear-induced crystallization, the group developed a robust method where a strong shear can be applied for a short time, thereby eliminating the reorienting effects of flow on the formed crystals (Liedauer, 1993). The experimental setup consisted of a rectangular slit having an aspect ratio of 1:10, mounted behind a single-screw extruder. A box-like pressure-time profile was created by pushing the polymer melt (iPP) through the slit for a short time, where the pressure was controlled by having an accumulator and bypass system attached to the extruder. Glass windows were installed at the duct, enabling in-situ observations to be made.
Figure 2.9. Experiment apparatus used by Liedauer et al. (1993) to investigate SIC.

The applied shear treatment was of medium strength, with the wall shear rates ranging from 60 – 140 s⁻¹. Crystallization was monitored by passing a polarized light through the sample and measuring the optical retardation with time (measurement starts after the short-time shear). After crystallization was complete, the sample was extracted from the duct and a cross-section parallel to the flow direction examined under the microscope. As seen in Figure 2.9, three distinct regions were observed: a highly oriented layer close to the duct wall, a finely-grained layer in the middle, and a spherulitic core.

Figure 2.10. Cross-section of an iPP sample extracted from the duct and then cut in the flow direction (Eder and Janeschitz-Kriegl, 1997).
The thickness of each layer depends on the shearing rate and duration used. In fact, for the shear-induced layers (the highly-oriented and finely-grained layers) to exist, there is a critical combination of shear rate and time – the weaker the shear, the longer the time needed to form the layer. A log-log plot of critical shear rate \( \dot{\gamma}_C \) vs. shearing time \( t_S \) shows a slope of -1/2 for the boundary between the fine-grained layer and the core, and -1/4 for that between the highly-oriented and fine-grained layers. This means:

For the fine-grained layer and core boundary: \( \dot{\gamma}_C^2 \cdot t_S = C_1 \)

For the highly-oriented layer and fine-grained layer boundary: \( \dot{\gamma}_C^4 \cdot t_S = C_2 \)

From these trends, Liedauer et al. (1993) proposed two subsequent nucleation steps in SIC:

1. Sporadic formation of spot-like primary nuclei with a frequency proportional to \( \dot{\gamma}^2 \) (assuming the simplest even function).
2. The transformation of a portion of the spot-like nuclei into “thread-like” precursors due to further shearing. These precursors are responsible for the formation of highly-oriented layer.

The two processes can be formulated as follows:

\[
\dot{N} = \left( \frac{\dot{\gamma}}{\dot{\gamma}_n} \right)^2 g_n \frac{N}{\tau_n} \\
\dot{L} = \left( \frac{\dot{\gamma}}{\dot{\gamma}_l} \right)^2 g_l \frac{L}{\tau_l}
\]

\( \dot{N} \) = rate of nucleation for the primary nuclei per unit volume.

\( \dot{L} \) = growth speed of the thread-like precursors.

\( \dot{\gamma}_n, \dot{\gamma}_l \) = characteristic shear rates for process (1) and (2), respectively.

\( \tau_n, \tau_l \) = relaxation times for process (1) and (2), respectively.

\( g_n \) = factor with dimensions \( m^{-3}s^{-1} \).

\( g_l \) = factor with dimensions \( ms^{-1} \).

By assuming \( \tau_n = \infty \) for the nuclei that grow into threads (i.e. the nuclei cannot disappear), an expression for the total length of precursors per unit volume, \( L_{tots} \), is obtained:
\[ L_{\text{tot}}(t_S) = g_n g_i \frac{\dot{\gamma}^4}{\dot{\gamma}_n^2 \cdot \dot{\gamma}_i} t_S^2 \]  
(2.11)

On the other hand, if \( \tau_l \) is assumed to be small compared with \( t_S \), another expression for \( L_{\text{tot}} \) comes up:

\[ L_{\text{tot}}(t_S) = 2 \frac{\dot{\gamma}^4}{\dot{\gamma}_n^2 \cdot \dot{\gamma}_i} g_n g_i \tau_l t_S \]  
(2.12)

Expressions (2.11) and (2.12) correspond to the empirical results that when \( L_{\text{tot}} \) is constant, \( \dot{\gamma}^4 \cdot t_S^2 \) or \( \dot{\gamma}^4 \cdot t_S \) is constant, respectively.

The investigation was then extended to iPP samples with other molecular parameters (Jerschow and Janeschitz-Kriegl, 1997). It was found that both long molecules and presence of nucleating agents enhances the formation of highly-oriented layer. In this case, the nucleating agent was so effective that the highly-oriented layer extends to the core of the sample, even at low shear rates.

Kumaraswamy et al. (1999, 2000, 2002) modified the “short-term shearing” method developed by the Linz group to enable more elaborate in-situ observations (e.g. light intensity, WAXD). They also found that a critical stress is required to induce formation of highly-oriented layer. However, beyond a critical shearing duration, the effectiveness of shear in speeding up crystallization seems to saturate, suggesting that the polymer chains have been oriented or stretched to the maximum extent.

The Linz group also contributed to the discussion on nucleation process, based on their experimental results (Janeschitz-Krieidl, 1997, and Janeschitz-Kriegl et al., 1999). By constructing a temperature-entropy \((T(S))\) diagram, they were able to estimate the temperature range of metastability, in which the primary mechanism of nucleation is sporadic or thermal. The molecular processes in this range are so sluggish, that without any help from flow, structure formation would not be noticeable. Below this range (i.e. at greater degrees of undercooling), only athermal nucleation takes place. The formation of well-defined and homogeneous spherulites often observed in quiescent, undercooled melt is the direct consequence of the latter nucleation type.
Recently, the group began several crystallization studies on PB-1 (Braun et al., 2003a, 2003b) using the same experimental method, with a particular emphasis on the nuclei formation in quiescent and shear-induced conditions. As in previous studies with polypropylene, the skin-core morphology of the sheared sample was found to be determined by the applied stress, or more appropriately, the amount of mechanical work done per unit volume. Relaxation experiments, where the melt is allowed to relax for a certain time after being sheared, showed that the relaxation time has a much greater dependence on temperature compared to the melt viscosity.

2.2.2 Elongational Flow

Compared to the amount of studies in shear-induced crystallization, those covering elongation-induced crystallization (EIC) are relatively few, despite its high relevance to processes such as fibre spinning and blow moulding. There are three types of elongational flow: uniaxial, biaxial, and planar, but only the first type will be considered for experiment in this thesis. Unlike in shear flow, it is much more difficult experimentally to develop a technique that is able to impose a pure uniaxial flow on the sample. Moreover, for crystallization experiments, the device must allow for a well-defined temperature protocol. Below, some of the important research in EIC is outlined by classifying the experimental method into three main types.

2.2.2.1 Melt Spinning

Early studies on EIC were mostly done in-line using a setup of extrusion and fibre spinning apparatus. The solidification of the fibre is observed as it comes out from the extruder, exposed by the cool air, and spun by the spinneret below. Pioneering papers in this area were given by Ziabicki and Kedzierska (1962), Nakamura et al. (1972), Dees and Spruiell (1974), and Spruiell and White (1975). The experiments generally use birefringence measurement and/or X-ray scattering on a running spinline, at various distances from the spinneret and with different spinning conditions.
As expected, elongational flow increased the crystallization rate and caused a change in the crystal morphology from spherulitic to rod-like. It was found that the spinline stress acts as the main factor that controls morphology development, and this in turn depends on many parameters like the difference between take-up and extrusion velocities, filament diameter, and surrounding temperature.

More recent studies include Laun and Schuch (1989), Samon et al. (2000), and Schultz et al. (2000). Samon et al. (2000) studied the melt spinning of PB-1 and observed that the take-up velocity influences the annealing time from Form II crystals (the metastable phase) into Form I crystals (the stable phase). In any case, this annealing time was significantly shorter compared to the melt crystallized in quiescent conditions.

Melt spinning remains an important experimental method due to its ability to simulate real processing conditions, with spinning speeds up to 8.3 m/s (Samon et al., 2000). However, with respect to the fundamentals in EIC analysis, the deformation and thermal histories are very complex. Since the process is highly non-isothermal, it is difficult to separate the influences of flow and temperature.
2.2.2.2 Flow Cells

Strong extensional flows can also be created by stagnation flows inside a flow cell. Several types of flow cell have been constructed by various researchers, for example the four-roll mill (Crowley et al. (1976), Dunlap and Leal (1987), Bushman and McHugh (1997)), opposed jets device (Mackay et al. (1995), Keller and Kolnaar (1997), Janeschitz-Kriegl et al. (2001)), and cross-slot device (Miles and Keller (1980), Gardner et al. (1982), Swartjes et al. (2003)). They have the same working principle: two liquid streams are impinged, resulting in a free stagnation point in the center that induces high extensional strain.

![Diagram of flow cells](image)

Figure 2.12. Several types of flow cell used to investigate elongation-induced crystallization: (a) lubricated converging flow, (b) cross-slot device, (c) opposed jets, (d) two-roll mill, (e) four-roll mill. (Swartjes, 2001).

In the study of Bushman and McHugh (1997), an HDPE-droplet was placed in an LLDPE carrier fluid, with the carrier staying in a melt state at the temperature of interest. A planar extensional flow was created inside the four-roll mill, and birefringence and dichroism measurements were performed to monitor the crystallization process. The results were used to construct a phenomenological model that takes into account the competing forces of crystallization and relaxation processes in determining the extent of molecular orientation. The viscoelastic molecular strain was predicted to be the controlling factor in flow-induced crystallization.
The opposing jets device used by Janeschitz-Kriegl et al. (2001) was originally introduced by Mackley and Keller (1973). Measurements were done with an iPP sample, and extension rates as high as 60 s\(^{-1}\) can be achieved in this device. However, it was found from this study that the design of the device was inadequate, because non-ideal flows were created at the outer parts of the fluid volume. Also in the cross-slot flow cell constructed by Swartjes (2001), there were shear gradients close to the observation windows in the cell, which made the flow a complex flow with a strong elongational component. Therefore, the search for the method(s) that are able to impose pure, uniaxial elongational flow continues and presents an interesting challenge for the study of EIC.

2.2.2.3 Extensional Rheometers

Extensional rheometers have been consistently used to measure the elongational viscosity of polymer melts, and they are also able to stretch the sample uniaxially, without any influences from shear flow. Two of the popular extensional rheometers were introduced by Münstedt (1979) and Meissner (1969).

Figure 2.13. Schematic of the oil-bath extensional rheometer designed by Münstedt (1979).
The Münstedt-type rheometer (Figure 2.13) uses an oil-bath to suspend the sample, compensate the gravity of the specimen by buoyancy (the density of the oil has to match that of the sample), and act as a heating liquid. The sample itself has a cylindrical form with a diameter of around 5 mm and length of 25 mm. Constant strain rate as well as constant stress (creep) experiments can be performed with this apparatus. While the range of strain rates $\dot{\varepsilon}$ achievable is quite wide (0.001 – 1 s$^{-1}$), the maximum Hencky strain $\varepsilon$ is limited to 3.8 by the height of the bath.

In the Meissner-type rheometer, the sample is plate-like in geometry (60 x 7 x 2 mm$^3$), and it is supported by a cushion of inert gas, also serving as a temperature controller. In the original version, the sample is placed horizontally and it is clamped on one end while the other end is drawn uniaxially. In the modified version like in Figure 2.14, (Meissner and Hostettler, 1993), extension is achieved by means of new type of clamps that make use of metal conveyor belts, attached at both ends of the sample. This rheometer type has the same range of strain rates like the oil-bath rheometer, but can achieve higher Hencky strains (up to 7). However, it cannot be used to perform creep tests.

![Figure 2.14. Schematic of the Meissner-type rheometer (Meissner and Hostettler, 1993).](image)

While these rheometers work very well for polymer melts and they have been shown to agree with each other (e.g. Münstedt et al., 1998), the set-up is rather bulky, which means that the cooling rates are generally too slow (around 1-2 °C) for crystallization studies.
Recently, Stadlbauer et al. (2004a, 2004b) from the Linz group developed a new version of extensional rheometer called Windbix (Figure 2.15). The device consists of a vertical expansion tube with a piston driven by pressurized gas, which is connected via two pulleys to the upper end of the sample in another tube. They conducted elongation flow-induced crystallization experiments using iPP sample and short-term stretching, from which it was found that even a small amount of work is already enough to result in a significant multiplication of nuclei. Okamoto et al. (1998a, 1998b) are the only ones so far who experimented with continuous stretching and performed a systematic approach concerning the influence of temperature and strain rate. In their case, PEN (poly(ethylene naphthalate)) and PET (poly(ethylene terephthalate)) samples were studied.

Figure 2.15. Schematic of the Windbix extensional rheometer (Stadlbauer et al., 2004). SH = sample hold, S = sample, L = laser, BD = birefringence detector, W = wire, G = glass tube, OP = overhead pulley, FT = force transducer, D = length transducer, PS = pneumatic stopper, Cu = top cover, Pi = piston, SI = slit.
Recently, an extensional tool consisting of dual wind-up drums was introduced by Sentmanat (2004). Another version was developed by TA Instruments and commercialized as the Extensional Viscosity Fixture (EVF). In this thesis, the latter device is used, which is installed as an add-on tool in the ARES rotational rheometer (more details are given in the Experimental section). Accurate temperature control and fast cooling/heating rates achievable in the ARES are therefore retained. Another advantage is the upright arrangement of sample strip, which reduces sagging. The small sample size (with a thickness of only 1 mm) also improves temperature homogeneity and reduces the time required for temperature equilibration.
3. EXPERIMENTAL PROCEDURE

3.1 Materials

3.1.1 Introduction on Polybutene-1 (PB-1)

Polybutene-1 (PB-1 for short), first synthesized by Natta (1955), is the youngest member of the polyolefine family, which includes the commodity products such as polyethylene (PE) and polypropylene (PP). The polymer has four carbon atoms on the backbone and is polymerized from the monomer butylene via a stereospecific mechanism, yielding an isotactic structure with 50-55% crystallinity (Ram, 1997). This polymer should not be confused with polyisobutylene (PIB), which is a synthetic rubber.

\[
\begin{align*}
\text{CH} & \quad \text{CH}_2 \\
\text{CH}_2\text{CH}_3 & \quad \text{Addition polymerization} \\
\text{CH}_2 & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_3 \\
\hline
\end{align*}
\]

Figure 3.1. Synthesis of PB-1 from butylene using addition polymerization method.

The crystallization kinetics of PB-1 is slower compared to PP or PE, thus facilitating an easier observation of crystallization progress under moderate undercoolings. Aside from the industrial interest from Basell as one of PB-1’s major manufacturers, this is one of the reasons that PB-1 was chosen for the project.

3.1.1.1 Physical and Chemical Properties

Listed in Table 3.1 are some typical properties of PB-1 (Kumar, 2003, Panse and Phillips, 2005, Azzurri, 2003).

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight of repeat unit, (M_0)</td>
<td>56.11 g/mol</td>
</tr>
<tr>
<td>Stereoregularity</td>
<td>95-99% isotactic</td>
</tr>
<tr>
<td>Thermal expansion coefficient, (\alpha)</td>
<td>(6.7 \times 10^{-4} \text{ K}^{-1})</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>Molar Heat Capacity, $C_p$ (at 100 °C)</td>
<td>110 J/mol.K</td>
</tr>
<tr>
<td>Heat of Fusion, $\Delta H_f$</td>
<td>7.8 kJ/mol</td>
</tr>
<tr>
<td>Thermal conductivity, $k$</td>
<td>0.22 W/m.K</td>
</tr>
<tr>
<td>Glass Transition Temperature, $T_g$</td>
<td>-25 °C</td>
</tr>
<tr>
<td>Equilibrium Melting Temperature, $T_m$</td>
<td>112 °C (Form II), 125 °C (Form I)</td>
</tr>
<tr>
<td>Crystallinity, $\alpha$</td>
<td>30% - 35% (Form II), 50% - 55% (Form I)</td>
</tr>
<tr>
<td>Density, $\rho$ (at 25 °C)</td>
<td>0.91 g/cm$^3$ (Form II), 0.95 g/cm$^3$ (Form I)</td>
</tr>
<tr>
<td>MFI (Melt Flow Index)</td>
<td>0.4-20 g/10 min (at 190 °C and 2.16 kg)</td>
</tr>
<tr>
<td>Tensile modulus, $\sigma$</td>
<td>290-295 MPa</td>
</tr>
<tr>
<td>Tensile strength at yield, $\sigma_y$</td>
<td>16-18 Mpa</td>
</tr>
<tr>
<td>Tensile strength at break, $\sigma_{break}$</td>
<td>32-35 Mpa</td>
</tr>
<tr>
<td>Notched Izod impact strength</td>
<td>640-800 J/m</td>
</tr>
<tr>
<td>Solvents (at above 100 °C)</td>
<td>Benzene, toluene, decalin, tetralin, chloroform, chlorobenzenes</td>
</tr>
</tbody>
</table>

One of the main advantages of PB-1 compared to other polyolefins is its excellent creep resistance. Its tensile modulus declines slowly with increasing temperature, and therefore it can withstand high temperatures, up to 100 °C. Like LDPE (low density polyethylene), PB-1 is ductile and tough, with excellent chemical resistance. The MSDS and product description sheets (from Basell) for the PB-1 grades used in the experiments can be found in Appendix A.

3.1.1.2 Polymorphism

Polybutene-1 has several crystalline modifications – this characteristic is termed polymorphism. Depending on the conditions under which it crystallizes, Corradini et al. (1976) classified five crystal forms for PB-1, listed in Table 3.2.
Table 3.2. Crystal modifications of PB-1 and their forming conditions. Forms I’ and II’ are the same as Forms I and II, respectively, only they exhibit lower melting temperatures and are achieved through different conditions.

<table>
<thead>
<tr>
<th>Form</th>
<th>Conditions</th>
<th>Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>By aging at room temperature and quiescent conditions</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>I’</td>
<td>Crystallization under high pressures or in certain solvents</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>II</td>
<td>Undercooled melt</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>II’</td>
<td>Pressure crystallization under controlled conditions</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>III</td>
<td>Crystallization in solvents</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

Form I and Form II are the most common ones encountered in processing. As Form I, PB-1 exhibits higher density, melting temperature, strength, rigidity, and turbidity compared to Form II. Some of these differences can be seen in Table 3.1. The chain conformation in Form I has 3 repeating units per 1 helix turn ($3_1$), while Form II has the conformation $11_3$ (less extended). Because of the changes in properties, it is very important for processing purposes that the factors affecting the transformation be known and quantified. At room temperature, the complete transformation from Form II to Form I (often called II→I transformation) takes around 10 days, but this depends further on factors such as molecular weight, molecular weight distribution, and comonomer content. This waiting time is disadvantageous for storage and product delivery, and therefore researchers seek the methods by which this time can be shortened. Azzurri (2003) performed the most recent comprehensive study on II→I transformation. In the past, many efforts have been done to study the effects of various parameters on the transformation, for example temperature (Danusso and Gianotti, 1965, Vidotto and Kovacs, 1967), pressure (Nakafuku and Miyaki, 1983), mechanical stress (Hong and Spruiell, 1985), molar mass (Schaffhauser, 1967, Chau and Geil, 1984), comonomeric units (Gianotti and Capizzi, 1969), and additives (Rubin, 1965, Hong and Spruiell, 1985).

The macroscopic morphology of the PB-1 crystallites itself (under quiescent condition) can take either spherulitic or hedritic form. The term “hedrites” for PB-1 was first introduced by Fu et al. (2001), who investigated the transition between the two
morphologies and found that it is a function of molecular weight and temperature. Acierno et al. (2002) also confirmed this behavior.

3.1.1.3 Processing and Applications
While PE and PP are produced in large quantities, the manufacture of PB-1 is small-scale in comparison. The 45 ktonne/year PB-1 production plant owned by Basell Polyolefins already accounts for the largest in the world, compared to the normal PE or PP outputs of more than 200 ktonne/year in some production plants (www.basell.com). Polybutene-1 is produced as a homopolymer or as a copolymer with ethylene content ranging from 0.75% to 5.5%. Because of its specialized applications, the price of PB-1 (around 3 US$/kg) is more expensive than PE or PP (around 1.1 US$/kg) (www.lme.com). The material can be processed easily like LDPE, including injection molding, extrusion, blow molding, rotational molding, thermoforming, and film blowing. Primarily, PB-1 is used to manufacture pipes for hot water delivery because of its excellent creep resistance and ability to withstand elevated temperatures. The second major application is as an additive for PE to produce easy opening packages. Other uses include hot melt adhesives, PP modifier, and niche applications.

![Figure 3.2. Examples of PB-1 product application: (a) hot water pipes, (b) seal-peel film, (c) food packaging (www.basell.com).](image)
3.1.2 Sample Characterization

All PB-1 samples were provided by Basell Polyolefins in Louvain-la-Neuve, Belgium, and were produced using the conventional Ziegler-Natta catalyst. Those having the suffix “M” were manufactured in the new Basell plant in Moerdijk, the Netherlands, while the others were from the Taft production plant in the U.S. The Moerdijk grades have narrower molecular weight distribution (MWD) and a slightly higher isotacticity compared to their Taft counterparts, but they are similar in molecular weight.

The samples with the highest molecular weights (BR200, PB0110, and PB0110M) were polymerized in the reactor and the grades with lower molecular weights were derived from these. BR200 and PB0110 have very similar molecular parameters, but PB0110 is nucleated with a small amount of HDPE (as also mentioned by Braun et al., 2003) whereas BR200 is non-nucleated. Then, to produce grades with lower molecular weights, these samples were extruded systematically to cut the long chain molecules (ex-Brabender). The extruded samples were derived from BR200 and therefore contain no nucleants.

Beside the homopolymer series, there are also two nucleated versions of BR200 (coded BR200-X1 and BR200-X2) and two poly(butene-1)-co-ethylene (C2C4) samples. Each of these will be described in more detail in the respective chapters relating to their crystallization behavior.

3.1.2.1 Molecular Weight Distribution

The molecular weight distribution of the samples was measured using Gel Permeation Chromatography (GPC), done in the Basell PP&C (Polymer Physics & Characterization) laboratory in Frankfurt, Germany, under the supervision of Dr. D. Lilge. In Table 3.3, the spectrum of samples is given with their respective molecular parameters.
Table 3.3. PB-1 samples provided by Basell Louvain-la-Neuve and used in the experiments. $M_w =$ weight average molecular weight, $M_n =$ number average molecular weight, $M_z =$ z-average molecular weight. The determination of molecular weight averages is based on universal calibration.

<table>
<thead>
<tr>
<th>Grade</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>$M_z/M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homopolymers, Taft grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BR200</td>
<td>762 000</td>
<td>19.6</td>
<td>3.2</td>
</tr>
<tr>
<td>PB0200</td>
<td>440 000</td>
<td>11.6</td>
<td>2.9</td>
</tr>
<tr>
<td>PB0300</td>
<td>305 000</td>
<td>8.7</td>
<td>2.4</td>
</tr>
<tr>
<td>PB0400</td>
<td>176 000</td>
<td>5.7</td>
<td>2.1</td>
</tr>
<tr>
<td>PB0800</td>
<td>133 000</td>
<td>4.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Homopolymers, Moerdijk grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB0110M</td>
<td>711 000</td>
<td>6.5</td>
<td>2.8</td>
</tr>
<tr>
<td>PB0300M</td>
<td>347 000</td>
<td>3.8</td>
<td>2.6</td>
</tr>
<tr>
<td>PB0400M</td>
<td>216 000</td>
<td>13.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Nucleated samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BR200-X1</td>
<td>668 000</td>
<td>8.4</td>
<td>3.2</td>
</tr>
<tr>
<td>BR200-X2</td>
<td>658 000</td>
<td>10.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Copolymers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP8010</td>
<td>876 000</td>
<td>10.3</td>
<td>3.1</td>
</tr>
<tr>
<td>DP8310</td>
<td>347 000</td>
<td>5.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The parameter $M_w/M_n$ (or $Q$) indicates the polydispersity index or PI, measured in polystyrene equivalents, while $M_z/M_w$ indicates the amount of long chain molecules in the sample, which is particularly important in flow-induced crystallization. The GPC curves are given in Appendix B.

3.1.2.2 Isotacticity

To determine the isotacticity of the samples, C$^{13}$ Nuclear Magnetic Resonance (NMR) analyses were performed by Basell PP&CC/ARC/NMR laboratory in Ferrara, Italy, under the supervision of Ms. I. Camurati. Table 3.4 lists the percentages of pentads [mmmm] for BR200 and PB0110M, which act as sources for other grades.
It can be seen that the Moerdijk grade (PB0110M) has a higher isotacticity than the Taft grade (BR200), and it also contains a small percentage of polyethylene, whether intended or as an impurity. All the lower molecular weight grades derived from these two sources have the same isotactcities, because the extrusion step does not change the stereoregularity of the sample. The nucleated samples have the same isotacticity as BR200, whereas for the C2C4 samples, NMR runs were performed but the $mmm$ cannot be determined because of the overlap between stereosequences and sequences. The NMR graphs can be seen in Appendix C.

### 3.1.2.3 Crystallization and Melting Points

The Differential Scanning Calorimetry (DSC) experiments were conducted to find the crystallization and melting points of the samples. Throughout this study, the nominal melting point ($T_m$) instead of the equilibrium melting point ($T_m^0$) will be used. This is chosen because $T_m$ is more practical as a benchmark in determining the degree of undercooling in crystallization experiments than $T_m^0$, which refers to zero heating rate and the melting of a perfect crystal. The peak values from the DSC curve are chosen to avoid ambiguity from the possible differences in the breadth of the endotherm (e.g. if the onset values were chosen instead and the degree of undercooling is to be measured).

The polymorphic characteristic of PB-1, as discussed in Section 3.1.1.2, directly affects the melting point. Form I has a higher melting point than Form II. Therefore, during DSC one has to be sure that the sample is composed only of either form. As explained before, Form II is obtained directly from cooling the melt, while a complete Form II to Form I transformation takes place after 10 days of storage under room temperature and pressure.
For each DSC run, only 5-6 mg of sample is required. First, the as-received sample is heated up to 200 °C to obtain the first melting point $T_{m1}$. Then, the melt is cooled to 25 °C to determine the crystallization point $T_k$. Lastly, the heating run is repeated to find the second melting point $T_{m2}$, which would correspond to Form II crystals. Unless mentioned otherwise, $T_{m2}$ will be used as the point of reference for the degree of undercooling throughout the thesis.

An example of a DSC run can be seen in Figure 3.3, whereas the DSC graphs for all the samples are included in Appendix D. In Table 3.5, the crystallization and melting points for the PB-1 samples are given. All the DSC runs were performed by Basell PP&C laboratory in Frankfurt, Germany, under the supervision of Dr. C. Gabriel.

![DSC graph]

Figure 3.3. DSC run on an as-received BR200 sample, with a heating/cooling rate of 10 K/min.

Table 3.5. Crystallization ($T_k$) and melting points ($T_{m1}$, $T_{m2}$) for as-received PB-1 samples, with heating/cooling rate of 10 K/min.

<table>
<thead>
<tr>
<th>Grade</th>
<th>$T_{m1}$ (°C)</th>
<th>$T_{m2}$ (°C)</th>
<th>$T_k$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR200</td>
<td>115.4</td>
<td>112.4</td>
<td>68.9</td>
</tr>
<tr>
<td>PB0110</td>
<td>117.9</td>
<td>114.3</td>
<td>84.0</td>
</tr>
<tr>
<td>PB0200</td>
<td>114.2</td>
<td>110.6</td>
<td>51.9</td>
</tr>
<tr>
<td>PB0300</td>
<td>113.4</td>
<td>111.4</td>
<td>58.0</td>
</tr>
</tbody>
</table>
Table 3.6. Crystallization ($T_k$) and melting points ($T_{m1}$, $T_{m2}$) for PB-1 samples stored for 10 days after crystallization from the melt. Heating/cooling rate is 10 K/min.

<table>
<thead>
<tr>
<th>Grade</th>
<th>$T_{m1}$ ($^\circ$C)</th>
<th>$T_{m2}$ ($^\circ$C)</th>
<th>$T_k$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR200</td>
<td>123.4</td>
<td>112.9</td>
<td>66.9</td>
</tr>
<tr>
<td>PB0110</td>
<td>127.1</td>
<td>114.8</td>
<td>83.6</td>
</tr>
<tr>
<td>PB0200</td>
<td>119.2</td>
<td>111.1</td>
<td>49.8</td>
</tr>
<tr>
<td>PB0300</td>
<td>120.6</td>
<td>111.7</td>
<td>57.0</td>
</tr>
<tr>
<td>PB0400</td>
<td>118.0</td>
<td>110.9</td>
<td>48.0</td>
</tr>
<tr>
<td>PB0800</td>
<td>116.8</td>
<td>108.3</td>
<td>56.3</td>
</tr>
<tr>
<td>PB0110M</td>
<td>124.0</td>
<td>115.6</td>
<td>69.3</td>
</tr>
</tbody>
</table>

For several samples, the heating/cooling cycle was repeated after 10-day storage under room temperature and pressure, in order to determine the melting point of Form I crystals. The results are shown in Table 3.6. Here, $T_{m1}$ and $T_{m2}$ refer to the melting points of Form I and Form II crystals, respectively. It is clear that the melting point of Form I is appreciably higher (about 8-10 °C) than Form II. The $T_{m2}$ values in Table 3.5 and 3.6 are consistent, which supports its choice as the point of reference for crystallization experiments.

Another factor which is important in DSC experiments is the applied heating/cooling rates. In Table 3.7, two other heating/cooling rates were tested to see the effects on $T_{m2}$.
and $T_k$. Apparently, there is only a slight, random variation on $T_m$, but $T_k$ decreases as the cooling rate is increased. This is reasonable because for fast cooling the sample has less time to crystallize properly. The rate of cooling will also affect the morphology of crystals formed. In fact, as mentioned in Braun et al. (2003), there is a critical cooling rate for each polymer type at which the melt will not crystallize, but form a glassy state instead. For PB-1, this would be around 25 °C/s (or 1500 °C/min).

Table 3.7. Effect of heating/cooling rate on crystallization and melting points for several as-received PB-1 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
<th>$T_k$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_k$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_k$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR200</td>
<td>112.2</td>
<td>78.3</td>
<td>112.4</td>
<td>68.9</td>
<td>111.6</td>
<td>61.9</td>
</tr>
<tr>
<td>PB0300</td>
<td>110.5</td>
<td>72.9</td>
<td>111.4</td>
<td>58.0</td>
<td>110.9</td>
<td>47.2</td>
</tr>
<tr>
<td>PB0400</td>
<td>109.3</td>
<td>68.7</td>
<td>110.7</td>
<td>51.4</td>
<td>110.1</td>
<td>52.5</td>
</tr>
<tr>
<td>BR200-X1</td>
<td>N/A</td>
<td>N/A</td>
<td>112.6</td>
<td>74.8</td>
<td>113.0</td>
<td>56.3</td>
</tr>
<tr>
<td>BR200-X2</td>
<td>N/A</td>
<td>N/A</td>
<td>114.2</td>
<td>88.1</td>
<td>114.4</td>
<td>84.0</td>
</tr>
</tbody>
</table>

3.1.2.4 Viscoelastic Properties

To assess the viscoelastic properties, Small Amplitude Oscillatory Shear (SAOS) experiments were carried out using ARES Rotational Rheometer from TA Instruments. The SAOS method probes material properties such as the storage and loss moduli ($G'$ and $G''$, respectively) and complex viscosity $\eta*$. For the experiments, discs of 25 mm diameter and 2 mm thickness were prepared by melting and pressing the granules in a Carver laboratory press at 180 °C for 5 minutes, with 5 kN force. The disc is annealed in the rotational rheometer to erase the temperature and flow histories, pressed to 1 mm thickness, and the spare material scraped off before the experiment is started.

Oscillatory shear runs were performed using an angular frequency range of $\omega = 0.01$-100 rad/s at four temperatures: 130 °C, 150 °C, 170 °C, and 190 °C. The measurements were done within the linear viscoelastic region of the samples. From the individual viscoelastic curves, a master curve is constructed using a TTS (Time-Temperature
Superposition) principle and an Arrhenius-type shift, which was found to be more suitable in all cases compared to WLF (William-Landel-Ferry) shift. Generally, the Arrhenius shift is valid for temperatures far above the glass transition temperature $T_g$, whereas WLF shift works for temperatures between $T_g$ and $T_g + 100$ (see Gedde, 1995, and Ferry, 1980). From this shifting procedure, the flow activation energy $E_a$ can be determined. An example of this master curve is given in Figure 3.4 for BR200.

![Figure 3.4. The viscoelastic master curve for BR200 ($T_{ref} = 150^\circ$C).](image)

In Table 3.8, several parameters describing the viscoelastic characteristics of the samples are listed. For some high molecular weight samples, it was difficult to determine $\eta_0$ since no plateau could be observed in the master curve. Actually, the lower frequency range could be expanded by measuring at even lower frequencies than 0.01 rad/s and/or at higher temperatures. However, problems arose because the measurement time for one data point was very long at low frequencies (e.g. at 0.001 rad/s, a point took 1 hour), while at temperatures higher than 220°C the PB-1 sample was degraded.

The equilibrium compliance (or steady-state recoverable shear compliance) $J^p_0$ was obtained by creep experiments using SR2 Rotational Rheometer from Rheometrics and the same sample thickness and size as in ARES. A constant stress of 50 Pa was applied,
and the sample response monitored over time. An example of creep experiment result can be seen in Figure 3.5.

Figure 3.5. Example of creep and creep recovery experiments for PB0110M, at 150 °C and with a constant stress of 20 Pa.

Table 3.8. Viscoelastic properties \((T_{ref} = 150 ^\circ C)\) of PB-1 samples (Index x denotes the cross over modulus or frequency. \(\eta_0 = \) zero shear viscosity, \(J'_x = \) equilibrium compliance, \(E_a = \) flow activation energy)

<table>
<thead>
<tr>
<th></th>
<th>(G'_x = G''_x) (kPa)</th>
<th>(\omega_x) (rad/s)</th>
<th>(\eta_0) (Pa.s)</th>
<th>(J'_x^0) (Pa(^{-1}))</th>
<th>(E_a) (kJ/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR200</td>
<td>9.4</td>
<td>0.32</td>
<td>2.3 x 10^5</td>
<td>4.28 x 10^{-4}</td>
<td>48</td>
</tr>
<tr>
<td>PB0110</td>
<td>9.8</td>
<td>0.23</td>
<td>2.6 x 10^5</td>
<td>3.80 x 10^{-4}</td>
<td>50</td>
</tr>
<tr>
<td>PB0200</td>
<td>14.5</td>
<td>2.9</td>
<td>3.2 x 10^4</td>
<td>3.30 x 10^{-4}</td>
<td>49</td>
</tr>
<tr>
<td>PB0300</td>
<td>18.1</td>
<td>9.9</td>
<td>1.1 x 10^4</td>
<td>2.27 x 10^{-4}</td>
<td>49</td>
</tr>
<tr>
<td>PB0400</td>
<td>24.0</td>
<td>70</td>
<td>1.8 x 10^3</td>
<td>1.64 x 10^{-4}</td>
<td>49</td>
</tr>
<tr>
<td>PB0800</td>
<td>25.2</td>
<td>180</td>
<td>7.6 x 10^4</td>
<td>3.54 x 10^{-4}</td>
<td>48</td>
</tr>
<tr>
<td>PB0110M</td>
<td>11.0</td>
<td>0.57</td>
<td>1.7 x 10^5</td>
<td>3.56 x 10^{-4}</td>
<td>50</td>
</tr>
<tr>
<td>BR200-X1</td>
<td>11.0</td>
<td>0.4</td>
<td>&gt; 2.2 x 10^5</td>
<td>N/A</td>
<td>45</td>
</tr>
<tr>
<td>BR200-X2</td>
<td>11.0</td>
<td>0.4</td>
<td>&gt; 2.4 x 10^5</td>
<td>N/A</td>
<td>48</td>
</tr>
<tr>
<td>DP8010</td>
<td>10.3</td>
<td>0.16</td>
<td>&gt; 3.9 x 10^5</td>
<td>7.81 x 10^{-4}</td>
<td>44</td>
</tr>
<tr>
<td>DP8310</td>
<td>19.1</td>
<td>8.6</td>
<td>1.8 x 10^4</td>
<td>5.76 x 10^{-4}</td>
<td>44</td>
</tr>
</tbody>
</table>
Most of the samples in Table 3.8 (excluding the nucleated samples and the copolymers) have very similar activation energies. This is expected, because the lower molecular weight grades were derived from one sample (BR200). Another way to see if the polymer samples belong in one series is by plotting the zero-shear viscosity against molecular weight in a double logarithmic scale (Figure 3.6), and check for a slope of 3.4 (Gedde, 1995). Considering the uncertainties associated with determining $\eta_0$ for high molecular weight samples, the data points in Figure 3.6 have an error of around 15%.

![Figure 3.6. Dependence of zero-shear viscosity on molecular weight for BR200 and other polymer grades derived from it.](image)

3.2 Devices

This chapter gives an overview of the devices employed in the crystallization experiments, focusing on the description of the device. Explanations on the specific experimental methods and the challenges involved are included in Chapters 4-6.

3.2.1 Quiescent / Quasi-Quiescent State

To investigate the crystallization kinetics of PB-1 in isothermal, quiescent state, two methods were used: rotational rheometry (oscillatory mode) and DSC. The ARES Rotational Rheometer from TA Instruments was used for the first method, and the
schematic of the device is given in Figure 3.7. The device is strain-controlled, and the temperature is regulated by blowing an inert (N₂) gas to the closed chamber. Two temperature sensors are available: one just below the lower plate, in the hollow shaft, and the other suspended in the chamber near the N₂ gas inlet. Only one sensor can be activated during an experiment. The first one was generally chosen because it measures the sample temperature accurately. The device operates with a Force Rebalance Transducer (FRT), which means that it measures the force or torque required to return the lower (rotating) plate to its starting position. Meanwhile, the sample gap is determined by adjusting the upper plate up and down. For most of the crystallization experiments, a 25 mm plate-plate setting was used with a final sample gap of 1 mm.

In the DSC experiments, the sample was melted at 180 °C for 10 minutes and then cooled to a temperature \( T \) below its melting point \( (T_{m2}) \). The sample was kept at this temperature, and when it started to crystallize, heat of crystallization was released and this was observable as the change in heat flow with time. The characteristic time of crystallization was then determined from the heat flow curve.

3.2.2 Shear-Induced Crystallization

3.2.2.1 ARES Rotational Rheometer

The ARES Rotational Rheometer was used extensively for shear-induced crystallization experiments in this study. Whereas the SAOS method was applied for quiescent...
crystallization runs, continuous shearing was the chosen mode to investigate shear-induced crystallization. The progress of crystallization was monitored from the increase in viscosity. However, as mentioned in Chapter 2: Literature Review section, the maximum shear rate that could be achieved in this device was limited to 1-2 s⁻¹. For higher shear rates, it was necessary to resort to other methods, as listed below.

3.2.2.2 Capillary Rheometer
One of the devices that were used to impose high shear rates (up to those encountered in extrusion process) was the capillary rheometer Rheograph 2003 from Göttfert, illustrated in Figure 3.8. In the crystallization experiments, a cylindrical die with a radius $R$ of 0.5 mm and length/radius ratio $L/R$ of 60 was fitted inside the rheometer. The cylindrical die has two small holes on the side, one at 2 mm from the top and the other at 2 mm from the bottom. The holes penetrate until 1 mm from the capillary. Temperature sensors can be inserted into these holes, and by this method the sample temperature as it enters and leaves the die was estimated. The temperature was found to be stable even at high shear rates (i.e. shear heating was not significant), with a temperature fluctuation of less than 0.5 °C. A pressure transducer is located just before the entrance of the die. After the device was properly heated up by an oil heating system, the sample was fed to the reservoir.

![Figure 3.8. A schematic of Göttfert capillary rheometer.](image-url)
When the sample was completely melted, a piston extruded the sample through the die with a set velocity, which corresponded to a certain shear rate depending on the size of the die. As crystallization set in, the capillary became blocked and an increase in pressure was observed. Therefore, the change in pressure with time was taken as a measure of the crystallization kinetics.

3.2.2.3 Concentric Cylinder Rheometer

Another method by which a high shear rate can be imposed is by using a concentric cylinder rheometer. This particular model (Figure 3.9) was developed in-house by BASF, and can achieve a torque up to 5 N.m. It consists of a cup and a bob, where the bob is driven by a motor and connected to a torque meter. The bob is held in its place with a metal cover, and in between there is a hollow cylinder made from fibreglass-reinforced Teflon that acts as an insulator. The bob has a diameter of 20.8 mm and the gap between the bob and the wall is 0.6 mm. The whole assembly is surrounded by an oil heating system. A special feature of the bob is that both the upper and lower surfaces form a 3° angle with the horizontal line. This was designed so that the system resembles a cone-plate setting, where a uniform shear rate is achieved everywhere in the chamber. The crystallization progress was monitored from the upshoot in the torque signal $M$. To check the sample temperature, it is possible to insert a temperature sensor into a cavity positioned 1 cm from the center. The hole goes until 1 mm from the base of the metal cover, the chamber under which is filled with the sample.

![Figure 3.9. The concentric cylinder rheometer.](image-url)
3.2.2.4 Multipass Rheometer (MPR)

The Multipass Rheometer was developed by the research group at Cambridge University in England under Prof. M. Mackley (www.cheng.cam.ac.uk/groups/polymer/MPR/index.html). The working principle behind this device is similar to a capillary rheometer, where the sample is driven through a die (slit or cylindrical). However, the MPR has several features that make it more versatile for research:

- It has two pistons instead of just one, enabling the sample to be pushed back and forth (hence “multi-pass”) through the die.
- Only a small sample volume is needed.
- There are observation windows for in-situ optical or X-ray analysis.
- An experimental temperature range from -20 °C (additional chiller required) to 200 °C.
- The system is fully enclosed, with a pressure limit of 200 bar.

The schematic of MPR is given in Figure 3.10(a), while the photo of the MPR equipped with an optical trail is shown in Figure 3.10(b). Two pressure transducers are fitted on top and below the die, and the rheological properties can be derived from the pressure measurements and capillary dimensions. The latest version (MPR IV) is available in BASF laboratory, and it is equipped with an optical trail to perform birefringence measurements. A slit die was used, with height = 1.5 mm, width = 10 mm, and gap for sample flow = 1 mm.
3.2.3 Elongation-Induced Crystallization

3.2.3.1 Extrusion + WAXS

One of the methods that was employed to study elongation-induced crystallization is the melt spinning experiment, where the sample is extruded and then drawn/spun with a certain speed. Such experiments were conducted, for example, by Spruiell and White (1975) on PE and PP samples and Samon et al. (2000) on PB-1. Depending on the extrusion and surrounding temperatures, drawing/spinning speed, and the material properties, the sample will crystallize as it is drawn. The X-ray is directed at a point along the fiber, and therefore the structure of the sample at this point can be analyzed.

Several trials were performed at the ESRF facility in Grenoble, France, with the help of Dr. Y. Men. A picture of the set-up can be seen in Figure 3.11. In this case, the extruded sample is drawn between two rotating wheels of a Göttfert Rheotens device. The distance from the extruder outlet to the center of the wheels was varied from 760-1000 mm. Three steel rods were placed at various heights to guide the fiber towards the wheels. The extrusion temperature and spinning speed were 160 °C and 100 m/s, respectively. These conditions were set so that the PB-1 melt has enough time to cool
down and crystallize before it reaches the wheels, to avoid the problem of melt sticking to the wheels. The X-ray beam was located at 20 cm above the wheels.

Figure 3.11. Experimental setup for extrusion + WAXS, showing the PB-1 fiber coming out from the extruder (top), guided by three steel rods (bottom left) and drawn by the Rheotens device (bottom right).

3.2.3.2 Meissner-type Rheometer (RME)

The Meissner-type Rheometer, first developed by Prof. J. Meissner in 1969 (Meissner, 1969) is often used to characterize the elongational viscosity of polymer samples. The sample has the form of a rectangular strip with dimensions of 60 x 7 x 2 mm³. The schematic of the device is already given in Figure 2.14, along with a short explanation of its operation (Section 2.2.2.3). For the crystallization experiments, the RME was
preferred compared to the Münstedt-type (oil bath) rheometer because of easier sample preparation and less bulky set-up.

3.2.3.3 Elongational Viscosity Fixture (EVF)

The Elongational Viscosity Fixture recently developed by TA Instruments (Figure 3.12) consists of two vertical cylinders arranged in parallel, between which a sample strip having dimensions of 18 mm x 10 mm x 1 mm is positioned at middle height using two clips. The EVF is attached to the ARES rotational rheometer, with one cylinder connected to the force transducer, and the other to the motor. The outer cylinder revolves around the inner one while rotating on its own axis, thereby stretching the sample uniaxially. A constant Hencky strain rate was applied for each experimental run by applying constant rotational speeds. Because the movement is limited to one full revolution, the maximum Hencky strain achievable in this device is limited to \( \varepsilon = 4.9 \) for a sample thickness of 0.7 mm. Practically, the maximum Hencky strain that could be achieved in the experiments was about 3.5 because the sample thickness was about 1 mm and the sample on the drums came in contact with itself before reaching one full revolution.

The temperature is regulated by blowing N\(_2\) gas into the chamber (forced convection). A temperature sensor, which acts as a feedback for the temperature controller, is located close to the inlet of the N\(_2\) gas. This location is 10 cm away from the centre of the sample. A temperature sensor closer to the sample, like that normally used for shear set-up in plate-plate or cone-plate geometry, is not available. Therefore, it is important to note that there is a distinct discrepancy between the chamber temperature \( T_{chamber} \) detected by the sensor and the actual sample temperature \( T_{sample} \). In steady-state condition, \( T_{sample} \) is always lower than \( T_{chamber} \), because there is a continuous heat loss through the shafts, which remain close to room temperature.
3.2.4 Morphology

3.2.4.1 Linkam Shear Cell

The Linkam CSS450 shear hot stage, shown in Figure 3.13, was used for in-situ morphology observation during crystallization. This device was developed by Mackley et al. (1999) of Cambridge University in England, and it basically operates with the same principle as a rotational rheometer with a plate-plate setup. The temperature is regulated by flowing oil through the upper and lower plates. Shear of certain magnitude can be imposed on the sample, but the device does not measure the viscosity of the sample. When the shear cell is attached to a microscope, the sample morphology can be observed directly through an observation window, which is located at 10 mm from the edge and has an observation radius of 7.5 mm. The pictures are then recorded by a CCD camera connected to a video recorder. Thin discs \(d \approx 150 \, \mu \text{m}\) were punched out from a pressed film and inserted between the two plates in the Linkam cell. At the melt state, the sample was slowly pressed to \(d = 70 \, \mu \text{m}\) so that a uniform thickness was obtained for each run. Also, pressing the sample prevented the sample from losing contact with the plates during cooling.
Two types of experiment were performed. The first one was concerned with crystallization in quiescent condition, where the sample was cooled down to crystallization temperature after annealing and left to solidify. In the second experiment type, shear was applied to the sample at crystallization temperature. When shearing continuously as is the case with ARES, problems often occur with the Linkam cell: when the viscosity increases due to crystallization, the torque becomes very large and the sample is damaged. To circumvent this, the sample was sheared only until close to the point where viscosity would shoot up, estimated from the results from ARES experiments.

3.2.4.2 Ex-Situ Light Microscopy

Ex-situ light microscopy for sheared or elongated samples were performed with assistance from Ms. G. Gille from the BASF Microscopy Department, under the supervision of Dr. W. Heckmann. The aim is to examine the crystal structure in the sample after it has crystallized under shear/elongation and retrieve information about the parameters that influence the transition from spherulitic (associated with quiescent condition or weak flows) to rod-like (associated with strong flows) structures.

Figure 3.13. Schematic side view of Linkam CSS450 Shear Cell attached to a microscope (left), and a top-side photo (right) ([www.linkam.co.uk](http://www.linkam.co.uk)).
3.2.5 Temperature Accuracy

Since the crystallization behavior of PB-1 is highly sensitive to temperature, it is important to test the temperature accuracies of each experimental method, especially because one of the main parameters investigated in this thesis (the crystallization onset time) obtained from different methods are later compared. Table 3.9 lists the temperature accuracies of the devices mentioned above. The tests were done by inserting temperature probes into the relevant sections in the devices (for example between the plates for the ARES Rheometer and in the chamber for the Concentric Cylinder Rheometer).

<table>
<thead>
<tr>
<th>Device</th>
<th>Temperature Accuracy (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARES Rotational Rheometer</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Capillary Rheometer</td>
<td>± 1</td>
</tr>
<tr>
<td>Concentric Cylinder Rheometer</td>
<td>± 0.5</td>
</tr>
<tr>
<td>MPR</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Extrusion + WAXS (in the extruder)</td>
<td>± 1</td>
</tr>
<tr>
<td>RME</td>
<td>± 0.5</td>
</tr>
<tr>
<td>EVF</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Linkam Shear Cell</td>
<td>± 0.5</td>
</tr>
</tbody>
</table>
4. QUIESCENT CRYSTALLIZATION

Before studying the crystallization behavior in flow-induced state, it is important to first understand how the sample crystallizes under quiescent conditions. As mentioned in Chapter 2: Literature Review, even in this simple situation there are challenges in understanding the mechanism of crystallization, in particular the nucleation stage. There are several recently proposed theories such as the mesomorphic layer formation by Strobl (2000) and spinodal decomposition by Terrill et al. (1998). These crystallization theories are based on the observation of change of physical properties in the sample. In this chapter, a quiescent/quasi-quiescent crystallization onset time, $t_{on,q}$, is introduced and the possible rheological methods by which this onset time can be determined are tested. Three experimental techniques using rotational rheometers were utilized for this purpose:

1. Small Amplitude Oscillatory Shear (SAOS),
2. Steady shear (with very small shear rate), and
3. Creep.

Since quiescent crystallization is the benchmark for studying more complex cases of crystallization under deformation, it is important to assess the reliability of these methods and to determine $t_{on,q}$ unambiguously.

The second aim of this chapter is to compare $t_{on,q}$ with another characteristic time that signifies a structural change in quiescent crystallization: the gel point $t_{gel}$. The experimental procedure developed by Mours and Winter (2000) was applied to obtain $t_{gel}$ at several temperatures.

Finally, the temperature dependence of these characteristic times in quiescent crystallization is investigated and compared for several PB-1 samples: PB0400, PB0300, BR200, BR200-X1, and BR200-X2. Acierno et al. (2002) studied the physical gelation of several PB-1 samples with varying molecular weights and similar molecular weight distribution. Their results indicate that the gel time is independent of molecular weight. In the current work it will be discussed whether the same trend is evident also for samples with different molecular weight distributions, and for samples that contain nucleating agents.
4.1 Sample Preparation and Temperature Protocol

4.1.1 Sample Preparation

The disc-shaped PB-1 samples used in ARES or SR2 rotational rheometer (plate-plate configuration was used in both cases) were prepared by pressing in a Carver laboratory press for 5 minutes at 180 °C with 5 kN force. The discs have a diameter of 25 mm and an initial thickness of 2 mm, pressed to 1 mm upon melting in the rheometer. The excess material was scraped off before the experiment started.

4.1.2 Temperature Protocol

Since PB-1 is a temperature-sensitive material and the crystallization kinetics depends strongly on temperature, a well-defined temperature protocol for the experiment is important for data reproducibility. The sample pre-treatment shown in Figure 4.1 applies for almost all the experiments using rotational rheometers. First, the sample was annealed at 180 °C for 10 minutes to ensure that any residual nuclei for crystallites were erased. This condition was proven to be sufficient to erase the flow and thermal histories, because higher temperature and/or longer annealing time did not bring a change in crystallization kinetics. Then, a constant cooling rate of -15 K/min was applied to the sample until the desired temperature was reached, for example $T = 101\ ^\circ C$. Time zero ($t = 0$) was chosen as the first instant the desired temperature was reached, and the experiment was started at this point. Because of the moderate cooling rate, the temperature undershoot which arose from this procedure was not more than 1.5 °C, and the temperature became stable after around 1 minute after $t = 0$. In the range of crystallization temperatures attempted here, the crystallization time was always longer than 1 hour, therefore it is safe to say that no significant crystallization occurred during the undershoot.
4.2 Quiescent/Quasi-Quiescent Onset Time Determination

4.2.1 Small Amplitude Oscillatory Shear (SAOS)

The pertinent method to measure changes of sample properties in quiescent crystallization is small amplitude oscillatory shear (SAOS), since this method exerts minimum disturbance to the sample. However, the chosen angular frequency $\omega$ and strain amplitude must be small enough not to speed up crystallization, and the combination must not exceed the linear viscoelastic region of the sample. Wassner and Maier (2000) employed this method in comparing the crystallization kinetics of polypropylene in quiescent and shear-induced conditions.

Then, the change in viscosity signal with time is monitored – at some point, the viscosity starts to increase significantly due to the crystallizing sample, and from here one can determine the quiescent crystallization onset time, $t_{on,q}$. In this case, the characteristic time is defined as the instant where $\eta(t_{on,q}) = 2\eta_{SS}$, where $\eta_{SS}$ is the steady viscosity value at the early stages of the experiment. An example is given in Figure 4.2, where the viscosity values are already normalized with respect to $\eta_{SS}$. The factor 2 is entirely arbitrary (for example, Wassner and Maier (2000) chose a factor of 10), but since the observed upturn in viscosity is sharp enough, no significant change on $t_{on,q}$ would be
expected if higher factors were chosen. In addition, a relatively low factor means that the sample has not gone too far from the initial (undercooled) melt state.

The SAOS runs were done using PB0400, with $\omega = 0.1$ rad/s and strain amplitude = 1% as the parameters. Four different temperatures were tested: 99 °C, 101 °C, 103 °C, and 105 °C, hence four different degrees of undercooling as measured from $T_{m2}$ of PB0400 (see Table 3.5). Figure 4.3 shows the experimental results, where it can be observed that $t_{on,q}$ decreases strongly with larger degrees of undercooling. From Figure 4.4, it can be seen that the reproducibility of this method is in the range of 10%, which is very good.

Figure 4.2. Determination of quiescent crystallization onset time for PB0400 at $T = 103$ °C.
Figure 4.3. Quiescent crystallization of PB0400 as measured by oscillatory shear at \( \omega = 0.1 \text{ rad/s} \) and strain amplitude = 1%, for temperatures 99-105 °C.

Figure 4.4. Reproducibility of SAOS runs for PB0400 at 101 °C
\( (\omega = 0.1 \text{ rad/s}, \text{ strain amplitude} = 1\%) \).

4.2.2 Continuous Shear
Continuous shear can also be used to probe the quiescent crystallization behavior of the sample, as long as the shear is small enough. More appropriately, this should be called a quasi-quiescent state, because actually the structure is disturbed by the continuous flow -
it is just that the polymer chains in the sample have enough time to relax despite the imposed orienting flow. This is clearly seen in Figure 4.5 for a series of steady shear experiments on PB0400 at 103 °C. As the shear rate is reduced, the upshoot in the viscosity curve is shifted towards longer times. However, below a certain shear rate (in this case 10^{-2} s^{-1}) there is no more rightward shift of the viscosity curve. As with the oscillatory shear method, the steady shear experiment also has an excellent reproducibility (Figure 4.6).

![Figure 4.5](image1.png)

**Figure 4.5.** Shear-induced crystallization of PB0400 at 103 °C, showing the limit of quasi-quiescent state for shear rates smaller than 0.01 s^{-1}.

![Figure 4.6](image2.png)

**Figure 4.6.** Reproducibility of quasi-quiescent steady shear experiment for PB0400 at 101 °C.
4.2.3 Creep

The third method to measure quiescent onset time is by performing creep experiment using SR2 rotational rheometer from Rheometrics. The only difference with ARES is that SR2 is stress-controlled instead of strain-controlled. In this case, a small constant stress of $\tau = 10$ Pa was continuously imposed on the sample, and the viscosity signal measured. Since the initial viscosity value for PB0400 is about 10000 Pa.s, this corresponds to a shear rate of $10^{-3}$ s$^{-1}$, which has been shown through Figure 4.5 to be small enough to achieve a quasi-quiescent state. In Figure 4.7, the reproducibility of this method is shown. As with the other two methods, a very good reproducibility is evident for the onset times.

![Figure 4.7. Reproducibility of creep experiments for PB0400 at 101 °C.](image)

4.2.4 Comparison of Results

In Table 4.1, the results from the three approaches to measure quiescent/quasi-quiescent onset time are compared. An oscillatory shear experiment performed using the SR2 is also included to ensure that this device produces the same result as with the ARES under the same experimental conditions. It can be concluded that there is an excellent agreement on the quiescent onset time obtained from the various methods, which is comparable with the reproducibility of each method. This fact shows that the quiescent
onset time is a well-defined parameter to characterize the quiescent crystallization process.

Table 4.1. Comparison of methods to measure quiescent crystallization of PB0400 at 101 °C.

<table>
<thead>
<tr>
<th>Device &amp; Method</th>
<th>Parameters</th>
<th>( t_{\text{on,q}} ) in minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARES Oscillatory</td>
<td>( \omega = 0.1 \text{ rad/s}, ) strain amplitude = 1%</td>
<td>160 ± 16</td>
</tr>
<tr>
<td>ARES Steady Shear</td>
<td>( \dot{\gamma} = 0.0001 \text{ s}^{-1} )</td>
<td>175 ± 18</td>
</tr>
<tr>
<td>SR2 Oscillatory</td>
<td>( \omega = 0.1 \text{ rad/s}, ) ( \tau = 10 \text{ Pa} )</td>
<td>185 ± 19</td>
</tr>
<tr>
<td>SR2 Creep</td>
<td>( \tau = 10 \text{ Pa} )</td>
<td>175 ± 18</td>
</tr>
</tbody>
</table>

While showing excellent agreement with each other, each method discussed in the previous section has its advantages. For example, with the steady-shear approach the shear rate can be increased progressively and the limiting shear rate that triggers shear-induced crystallization at a certain temperature can be directly estimated. On the other hand, for different samples one has to test at least several shear rates to be sure that the plateau region is reached. The SAOS approach is generally considered to be less disruptive for the sample, because the sample is sheared very slightly in two directions instead of continuously in one direction. Therefore, the total strain in the sample is less for the SAOS approach. With the creep experiment using SR2, a very small constant stress can be applied, which may result in a smaller shear rate value than that achievable by the ARES (the lower limit is \( 2.5 \times 10^{-5} \text{ s}^{-1} \)), depending on the viscosity of the sample. The creep method is therefore appropriate for samples with high viscosity, where a condition closer to the quiescent state will be achieved.

4.3 Gel Time Determination

4.3.1 Definition of Gel Time

The theory of physical gelation was introduced by Winter and Mours (1997) as the stage where there is a transition from liquid to solid state, and it is envisioned that during this process there is an increased connectivity of the structures evolving in the sample. Although it is difficult to track this process visually, a well-developed rheological method is able to probe the change in sample properties during gelation and thus determine the gel point with reasonable accuracy. This method was first developed for crosslinking
polymers (i.e. chemical gelation) by Winter and Chambon (1986), but the same principles were later proved to be applicable for physical gelation (Schwittay et al., 1995).

Pogodina et al. (2001) compared the time scales of this gelation process with morphological and optical changes for a sample of isotactic polypropylene (iPP). In their study it was concluded that the defined gel point occurs earlier than the impingement of spherulites and the point of maximum density fluctuations as measured by SALS (Small Angle Light Scattering). The absolute crystallinity at the gel point has been estimated to be between 12-17%, although in an earlier paper (Pogodina and Winter, 1998) a much lower value (around 2%) was reported (a different method was used for the determination of crystallinity). In any case, at the gel point a relatively small crystallinity is expected.

4.3.2 Cyclic Frequency Sweep (CFS)

The gel time determination was performed following the guidelines described by Mours and Winter (2000), using a method called Cyclic Frequency Sweep (CFS). In this method, successive sweeps within a certain angular frequency range are performed continuously to capture the evolution of moduli ($G'$ and $G''$) and consequently of loss tangent $\tan \delta$. An example of how the moduli values change during gelation can be seen in Figure 4.8 for PB0400. In this example, the gel point occurs at $t_{gel} = 250$ minutes. At this time, there is a significant change in shape in the low frequency region for the $G'$ vs. $\omega$ curve (Figure 4.8(a)), but not for the loss modulus curve. Hence, the storage modulus is more sensitive as an indicator of the gelation process.
However, \( t_{gel} \) is usually deduced from \( \tan \delta \) instead of \( G' \) plot. There are two ways to do this: from a frequency-dependent plot (where a plot of \( \tan \delta \) vs. \( \omega \) shows a flat part in the low frequency region) and from a time-dependent plot (where the curves of \( \tan \delta \) vs. \( t \) from different angular frequencies intersect). In this study, the latter approach is adopted, as can be seen in Figure 4.9.
4.3.3 Limitations

Because the $t_{gel}$ determination depends on the frequency range chosen, it is important to consider the two limiting factors for the selection of angular frequency range: the flow regime of the polymer and the measurement time for a single data point. Firstly, the $\tan \delta$ values measured at the selected frequencies should be significantly larger than 1 at the start of the experiment. When $\tan \delta$ is close to or even lower than unity, only the response resulting from the entanglement network will be obtained, which is not sensitive to the early stages of crystallization. Secondly, the measurement time for a single data point has to be small enough compared to the change of sample properties during that time. The Mutation Number $N_{Mu}$ assesses the condition of quasi-stability during the measurement, and it is defined by Mours and Winter (2000) as the following:

$$N_{Mu} = \frac{\text{experimental time}}{\text{mutation time}} = \frac{\Delta t}{\lambda_{Mu}}, \quad (4.1)$$

where

$$\Delta t = \left( \frac{2\pi}{\omega} \right) \times \text{number of cycles per data point, in s} \quad (4.2)$$

and

$$\lambda_{Mu} = \left| \frac{1}{dG'} \frac{dG'}{dt} \right|^{-1}, \text{ in s} \quad (4.3)$$

The parameter $G'$ is chosen as the basis to calculate $N_{Mu}$, since it is more sensitive than $G''$ and thus provides a safer limit of quasi-stability. The upper limit for $N_{Mu}$ is rather arbitrary. Pogodina and Winter (1998) used a limit of 0.3 in their experiment, and Schwittay et al. (1995) mentioned a limit of 1 for quasi-stability. In this study a limit of $N_{Mu} < 1$ is used.

It must be noted that the two limitations mentioned above contradict each other. The first requirement recommends using a low frequency range to be safely in the flow region, but as the angular frequency becomes lower, the measurement time becomes significantly longer.
For PB0400, a good balance between the two requirements is obtained in the frequency range of 0.1-0.05 rad/s. This range is two orders of magnitude lower than the crossover frequency at 107 °C (see Figure 4.14), which means that it should be safely in the flow region. A data point at 0.05 rad/s takes roughly 5 minutes. In the temperature range of 99-107 °C, the crystallization rate of PB0400 is slow enough to allow $N_{_M}$ to be less than one at this frequency. Therefore, three frequencies were chosen within this range: 0.1, 0.07, and 0.05 rad/s. An example of $t_{gel}$ measurement is given in Figure 4.9 for PB0400 at three temperatures.

The reproducibility of the gel time measurements is not as good as that obtained from the quiescent onset time measurements. In addition to experimental scatter, there is some reading error involved in determining the crossover point of the frequency curves. Therefore, it is estimated that the reproducibility of the runs is 15%.

![Figure 4.9. Gel time for PB0400 at three temperatures.](image)

### 4.4 Comparison between $t_{on}$ and $t_{gel}$

The results from gel time measurements can also be applied to estimate the quiescent onset time, since these measurements are actually no other than SAOS runs at three angular frequencies. Hence, the moduli values can be converted into complex viscosity values, which can then be used to estimate $t_{on,q}$. An example is given below.
Figure 4.10. Converting data from (a) $t_{gel}$ measurement to (b) $t_{on,q}$ measurement from the same experimental run (PB0400 at 101 °C).

Figure 4.10 shows that $t_{gel}$ and $t_{on,q}$ are very close to each other, at least at this temperature. There is less arbitrariness involved in determining $t_{on,q}$, as seen from its independence from the angular frequency used, whereas in $t_{gel}$ estimation the selection of angular frequency is important and can cause an observable shift in the crossover value.
The relationship between $t_{on,q}$ and $t_{gel}$ is investigated further by comparing the two quantities at different temperatures (Figure 4.11). The blank diamonds refer to the $t_{on,q}$ data obtained from independent SAOS measurements (data from Figure 4.3), and the filled diamonds are plotted using the same data from $t_{gel}$ measurements, just like in Figure 4.10. Although there is a significant gap between the two series, both show a general trend that the ratio of $t_{on,q}/t_{gel}$ at higher temperature is larger than at lower temperature. From the graph a conclusion can be drawn that $t_{gel}$ occurs earlier than $t_{on,q}$, but the two parameters have different temperature dependencies.

This fact is reasonable because $t_{gel}$ and $t_{on,q}$ correspond to different phenomena in crystallization process. The gel point, as also confirmed by Pogodina et al. (2001) occurs after spherulites become visible but before they impinge – these spherulites act as crosslinking points in the network that still contains a significant amount of amorphous melt. As mentioned before, Pogodina et al. (2001) estimated the absolute crystallinity at gel point to be quite low. The quiescent onset time, on the other hand, is obtained from the upshoot in viscosity signal, which is very likely to occur near the time when spherulites impinge. An example of comparison between morphology development and

Figure 4.11. Comparison of $t_{on,q}$ and $t_{gel}$ for PB0400 at 99-105 °C. The blank diamonds use $t_{on,q}$ data from independent SAOS measurements and the filled diamonds use $t_{on,q}$ data from $t_{gel}$ experiments.
the viscosity curve during crystallization is included in Chapter 4.5 and can also be seen in Hadinata et al. (2005).

4.4.1 Effect of Molecular Weight Distribution

After comparing the different methods to characterize quiescent crystallization, it is interesting to investigate how the characteristic times ($t_{on,q}$ and $t_{gel}$) are influenced by the molecular parameters of the sample. For this purpose, three PB-1 samples were selected: PB0400, PB0300, and BR200. The molecular and viscoelastic properties of these samples can be seen in Tables 3.3 and 3.7, respectively. Figure 4.3 already shows that there is a strong dependence of $t_{on,q}$ on temperature. In fact, as plotted in Figure 4.12 for PB0400, this dependence is exponential in the range of temperatures (below $T_{m2}$) considered. If one goes closer to $T_{m2}$, $t_{on,q}$ will approach infinity. In Figure 4.12, another parameter $\Lambda$, the characteristic retardation time, is included. This parameter describes the decay of orientation in the melt and depends on the chain length of the polymer (by the zero shear viscosity) as well as on the breadth of the molecular weight distribution (by the equilibrium compliance):

$$\Lambda \equiv \eta_0 J_e^0$$  \hspace{1cm} (4.4)

The equilibrium compliance is assumed constant for the temperature range considered here, while $\eta_0$ follows an Arrhenius dependence (the flow activation energies $E_a$ for the PB-1 samples are given in Table 3.7).

$$\Lambda(T) = J_e^o \eta_0 (T_o) \exp \left[ \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_o} \right) \right]$$  \hspace{1cm} (4.5)

Evidently, from Figure 4.12 the temperature dependence of $\Lambda$ in the experimental range is much weaker compared to that of $t_{on,q}$. The significance of $\Lambda$ will become more apparent in Chapter 5: Shear-Induced Crystallization.
Figure 4.12. The dependence of quiescent onset time $t_{on,q}$ and characteristic retardation time $\Lambda$ on temperature for PB0400, in $T$ range 99 °C – 107 °C.

The $t_{on,q}$ vs. $T$ trend in Figure 4.12 follows the exponential law:

$$t_{on,q} = C_1 \exp[n_1 T] \quad (372 \ K \leq T \leq 380 \ K), \quad \text{(4.6)}$$

where $C_1 = 6 \cdot 10^{-54} \text{ s}$, $n_1 = 0.35 \text{ K}^{-1}$, $R^2 = 0.9876$

or expressed in degrees of undercooling:

$$t_{on,q} = C_2 \exp[n_2 (T_{m2} - T)], \quad \text{(4.7)}$$

where $C_2 = 5 \cdot 10^5 \text{ s}$, $n_2 = -0.35 \text{ K}^{-1}$

Equations 4.6 and 4.7 are valid for $T < T_{m2}$, otherwise they fail because $t_{on,q}$ will be infinite. When this $T$-dependence of $t_{on,q}$ is compared for the three samples in the same temperature range, the result can be seen in Figures 4.13(a) and (b). The systematic shift to shorter onset times as molecular weight increases, which is apparent in Figure 4.13(a), does not show when the onset times are plotted against degree of undercooling, $T_{m2} - T$ (Figure 4.13(b)), and all the data points can be reasonably fitted by one trendline:

$$t_{on,q} = C_3 \exp[n_3 (T_{m2} - T)], \quad \text{(4.8)}$$

where $C_3 = 2.2 \cdot 10^5 \text{ s}$, $n_3 = -0.36 \text{ K}^{-1}$, $R^2 = 0.9360$
Figure 4.13. Quiescent onset times for PB0400, PB0300, and BR200 as a function of (a) temperature, and (b) degree of undercooling.

It is pertinent to ask whether $t_{gel}$ will exhibit the same behavior. A study by Acierno et al. (2002) compared $t_{gel}$ for different PB-1 samples at one crystallization temperature ($103 \, ^\circ\text{C}$). The samples used in their study have a similar distribution but different average molecular weights. In the present case, the distributions of the samples also differ (Table 3.3). Especially, BR200 has a significantly broader distribution and also a higher weight average molecular weight ($M_w$) compared to PB0400 and PB0300.
This high molecular weight of BR200 makes it difficult to determine the gel point with the method described earlier. The reason can be seen in Figure 4.14, which shows the moduli curves for the three PB-1 samples at 107 °C. As mentioned, for the gel point determination one needs to have an angular frequency range that is quite far in the flow region. For BR200, this means having angular frequencies lower than the crossover frequency $\omega_c$ of 0.06 rad/s. Meanwhile, the measurement time required for a single data point becomes very long in this area. For example, at 0.01 rad/s the machine needs 20 minutes for one data point. In the temperature range considered (99-107 °C), the $N_{Mu}$ value will exceed unity for such a long measurement time. Therefore, it is concluded that the gel time for BR200 cannot be determined using this method. Trials with a frequency range of 0.1-0.05 rad/s only resulted in initial $\tan \delta$ values of around 1, which are not sufficient to characterize the gel point.

![Figure 4.14. Moduli data from oscillatory measurements at 107 °C for PB0400, PB0300, and BR200.](image)

This leaves PB0400 and PB0300 to be compared. Even for PB0300, lower initial $\tan \delta$ values are expected when the same angular frequency range (0.1-0.05 rad/s) is used. Indeed, the initial $\tan \delta$ values for PB0300 are between 2 and 4 for the temperature range studied (i.e. close to the limit of flow region), whereas for PB0400 they are between 6 and 14.
Figure 4.15. Comparison between the gel times for PB0400 and PB0300, using (a) the same angular frequency window and (b) the same initial $\tan \delta$ values.

Therefore, the effect of angular frequency window selection has to be taken into account in comparing the gel times of PB0400 and PB0300. In Figure 4.15(a), the gel times of both samples measured using the same angular frequency window are shown. The symbol $\Delta T$ refers to the difference between $T$ and $T_m$. In Figure 4.15(b), the angular frequency window for PB0400 was adjusted so that the initial $\tan \delta$ values are similar as
those for PB0300. In performing these experiments over a range of temperature for one sample, the same angular frequency window is kept. There is a slight variation in initial $\tan \delta$ values when the temperature is increased from 99 °C to 107 °C, for example, but this does not change the $t_{gel}$ value substantially.

Figure 4.15(b) shows that the gel time dependency on temperature for PB0400 and PB0300 is the same, which supports the trend found with $t_{on,q}$ and the findings by Acierno et al. (2002) that $M_w$ has no effect in quiescent crystallization process. The trend in Figure 4.15(b) follows an exponential law:

$$t_{gel} = C_4 \exp[n(T_{m2} - T)] \quad (372 \text{ K} \leq T \leq 380 \text{ K}) \quad (4.9)$$

$$C_4 = 1.5 \cdot 10^5 \text{ s}, \quad n = -0.29 \text{ K}^{-1}$$

This corresponds to the earlier observation with PB0400 (Figure 4.11), where $t_{on,q}$ increases more quickly with temperature (hence a steeper slope) compared to $t_{gel}$. Since the error in the experimental data ($t_{on,q}$ or $t_{gel}$) is quite small (10%), this would not significantly affect the slopes of the fit, and the exponential values are reliable.

### 4.4.2 Effect of Isotacticity

Experiments with shear rate of $10^{-4}$ s$^{-1}$ (quasi-quiescent condition) and different degrees of undercooling have also been done for BR200 and PB0110M, which have different isotacticity levels but similar molecular weights (Tables 3.3 and 3.4). At 107 °C and quasi-quiescent condition, the crystallization onset time of BR200 was found to be 10 hours, three times longer than that of PB0110M (3.3 hours), although the melting points of the two samples only differ by 3 °C (Table 3.5). The higher melting point of PB0110M is attributed to its higher isotacticity, because more regularity in the chain results in a rise in the melting point. However, when the quiescent onset times are plotted against degree of undercooling, both samples show the same temperature dependence, as can be seen in Figure 4.16.

The data points can be fitted with an exponential function as follows:

$$t_{on,q} = 4 \cdot 10^5 e^{-0.3964(T_{m2} - T)} \quad (4.10)$$
Figure 4.16. Crystallization onset time at $10^{-4}$ s$^{-1}$ for BR200 and PB0110M as a function of degree of undercooling.

From this equation and taking an example of $T = 85$ °C, the expected quiescent onset times would be 8 s for BR200 and 2 s for PB0110M. When crystallization half-time experiments were performed using DSC at $T = 85$ °C, the heat of crystallization curves for the two samples can be seen in Figure 4.17(a) and the converted crystallization curves in Figure 4.17(b). The times required to reach 50% of fully crystallizable material are 4.5 minutes and 3 minutes for BR200 and PB0110M, respectively. These times are orders of magnitude greater than the expected quiescent onset times at the same temperature, following the equation above, which in turn was determined from viscosity measurements. This seems to suggest that the increase in viscosity corresponds only to a small degree of crystallization.
Figure 4.17. (a) Heat of crystallization curves for BR200 and PB0110M from DSC measurements at 85 °C, and (b) the corresponding degree of crystallization curves.

4.4.3 Effect of Nucleants

In this section, the effects of nucleating agents on the quiescent crystallization behavior were investigated using BR200 and its two nucleated variants, BR200-X1 and BR200-X2. The first variant is nucleated with 1000 ppm HDPE, while the second with 1000 ppm EBS. Generally, the expected influence (and purpose) of nucleants is to enhance the crystallization process by providing extra nucleation sites or reducing the kinetic energy.
barrier for the chains to fold themselves (Feng et al., 1997). In addition, nucleants may also affect the morphology of the formed crystals.

It is shown in Table 3.3 that the molecular weights of the nucleated samples are similar to that of BR200, but both are more narrowly distributed. However, in Section 4.4.1 it has been shown that differences in molecular weight and/or distribution should not affect quiescent crystallization behavior, if measured at the same degrees of undercooling. Therefore, in this case any differences in behavior can be attributed to the presence of nucleating agents. Compared with pure BR200, the HDPE-nucleated sample (BR200-X1) has higher $T_{m1}$ and higher $T_k$, but the value of $T_{m2}$ is practically the same (see Table 3.5). For the EBS-nucleated sample (BR200-X2), $T_{m1}$ and $T_{m2}$ show a 2 °C increase from BR200, while the increase in $T_k$ is much larger. The enthalpy for BR200 is slightly higher than the nucleated samples, both for the first and second heating runs. As with previous measurements, $T_{m2}$ is used as a reference to measure the degree of undercooling since it refers purely to Form II crystals, obtained directly after solidification from the melt.

As for the viscoelastic properties, the presence of nucleants does not have any observable effects, as evident from Figure 4.18 for a reference temperature of 150 °C.

![Viscoelastic properties mastercurves at $T_{ref.} = 150$ °C for BR200 (blank symbols), BR200-X1 (black symbols), and BR200-X2 (grey symbols).](image)

Figure 4.18. Viscoelastic properties mastercurves at $T_{ref.} = 150$ °C for BR200 (blank symbols), BR200-X1 (black symbols), and BR200-X2 (grey symbols).
Quasi-quiescent experiments were also performed on the nucleated samples by shearing at $10^{-4}$ s$^{-1}$. In Figure 4.19, $t_{on,q}$ is plotted against the degree of undercooling, $T_{m2} - T$, for the three samples. The onset times show an exponential dependence on temperature for all three samples. With BR200 and BR200-X1, a difference in onset times is only found for 99 °C, which seems to indicate that HDPE as a nucleating agent is more effective at low temperatures. From the morphology pictures (see Section 4.5), however, there is no noticeable difference in spherulitic growth at 99 °C for these two samples. On the other hand, for BR200-X2, the line is shifted downwards by more than factor of 20, which means that its crystallization kinetics under quiescent conditions is much faster compared to the other two samples. Therefore, EBS is more effective than HDPE in enhancing the quiescent crystallization kinetics.

![Figure 4.19. Quasi-quiescent onset times for BR200 and the nucleated versions at 99 °C, 103 °C, and 107 °C.](image)

4.4.4 Effect of Copolymer Content

To investigate quiescent crystallization for the C2C4 samples (DP8010 and DP8310), the experiments were conducted at a much lower temperature range: 70 – 80 °C for DP8010 and 80 – 90 °C for DP8310, owing to their low $T_{m2}$ values compared with the homopolymers. It is interesting that an ethylene comonomer content of just 5.5% can trigger a 20 – 30 °C drop in the melting point and a large reduction (around 30 J/g) in the
heat of fusion. The resulting quiescent onset times are compared with those from the homopolymers having similar molecular weights (DP8310 - PB0300, and DP8010 – BR200), as can be seen in Table 3.3. In Figure 4.20(a), the onset times are plotted against temperature, while in Figure 4.20(b), they are plotted against degree of undercooling (taking $T_{m2}$ as the benchmark).

The following trends can be observed for the quiescent crystallization of the C2C4 copolymers:

- There is an exponential temperature dependence, just like the case for homopolymers, but with weaker slopes. It suggests that a different crystallization mechanism prevails, in which less perfect crystals are formed (also shown by DSC data for the copolymers).

- The two copolymers exhibit different temperature dependences between themselves, although both contain 5.5% ethylene and only differ in molecular weights. Therefore, the previous conclusion that molecular weight distribution does not affect quiescent crystallization is not valid for the copolymers.

- Below but close to $T_{m2}$, quiescent crystallization still proceeds relatively fast compared to the homopolymers, as can be seen clearly from Figure 4.20(b).
4.5 Morphological Observations

Morphological observations on quiescent crystallization were made using the Linkam cell and by punching out thin discs ($d \approx 150 \mu m$), as described in more detail in Section 3.2.4.1. It is important to note that the experiments were performed under a truly quiescent condition (i.e. no flow at all) in the Linkam Cell, whereas for the viscosity curves and onset time determination using ARES a very weak flow (normally a shear rate of $10^{-4} s^{-1}$) was still involved (i.e. a quasi-quiescent state). When the pictures from Linkam Cell experiments are compared with the viscosity curve on the same time scale, the results can be seen in Figures 4.21(a) for PB0400 and (b) for BR200.

Spherulitic growth was observed for both PB0400 and BR200. In Figure 4.21(a), at the moment when the first crystallites start to be visible - a large part of the sample remains amorphous - viscosity has already risen by 10%. As discussed previously in Section 4.4.2, however, this increase is likely to correspond to only a minimal degree of crystallization. Eventually, the viscosity exhibits a sharper upturn as spherulites begin to impinge and more space is occupied by the growing crystal. In Figure 4.21(b), impingement is not observed near the viscosity upturn. This might be due to a case of an
isolated spherulite, and it is possible that impingements may occur at other sites across the sample at this point in time.

To see the effect of nucleants on the crystallization kinetics and morphology in quiescent condition, several runs were also conducted for BR200-X1 and BR200-X2. Because these samples have high molecular weights and therefore tougher to press, the discs were slightly thicker, about 250-350 µm. When the sample had been melted, the gap in the
Linkam Cell was still set to the same distance of 70 µm like other samples. Figures 4.22(a)-(c) show the quiescent crystallization at 99 °C for BR200, BR200-X1, and BR200-X2. It can be seen that BR200 and BR200-X1 have the same behavior; they developed large spherulites in a similar time scale, and by around 30 minutes most of the spherulites already impinged on each other.

Figure 4.22. Development of crystallites in quiescent condition at 99 °C for (a) BR200, (b) BR200-X1, and (c) BR200-X2.
For BR200-X2, however, a large number of tiny crystals were formed very quickly and filled the space. Because of their size, it is difficult to determine if they also have spherulitic shape, and after 5 minutes no change in the area of observation could be detected further. The reduction of spherulite size is often the purpose of adding nucleants, and here it is proven from that EBS works effectively as a nucleating agent.

4.6 Chapter Conclusions
Two characteristic times relevant in quiescent crystallization have been compared in this study: quiescent onset time $t_{on,q}$, measured from the viscosity upshoot during crystallization, and gel time $t_{gel}$, measured from the change in $\tan \delta$. It was found that for PB0400, in a range of crystallization temperatures, $t_{gel}$ always occurs earlier than $t_{on,q}$, but they exhibit different temperature dependences. The gel time detects an earlier crystallization stage where tiny spherulites act as crosslinks in an amorphous matrix, and this can be compared with other methods that are also related to early crystallization stages, such as SALS. Meanwhile, the quiescent onset time is measured from the viscosity upshoot, which can be associated with impingement of spherulites, i.e. a more advanced stage of crystallization.

When samples having different molecular parameters are involved, $t_{on,q}$ is more robust than $t_{gel}$ as a quantitative tool to compare their crystallization behavior. Gel time measurements have to be done in the flow region, and for samples with high average molecular weights this is technically difficult. On the other hand, $t_{on,q}$ can be determined by several methods: Small Amplitude Oscillatory Shear (SAOS), steady shear, and constant stress (creep) experiments. The two latter approaches actually simulate only a quasi-quiescent state since a continuous flow is imposed on the sample. However, in the limit of very small shear rate or stress, the polymer chains have enough time to relax and crystallization progresses as in a quiescent condition. With the steady-shear method, by trying several shear rates one has the advantage of knowing at which shear rate does shear-induced crystallization (SIC) begin to take effect. Therefore, this approach was also used in the SIC experiments.
The effects of molecular weight ($M_w$) and weight-average molecular weight distribution ($M_w/M_n$) on $t_{on,q}$ and $t_{gel}$ have been covered for three PB-1 samples: PB0400, PB0300, and BR200. Apparently, the variation of $t_{on,q}$ with $M_w$ and $M_w/M_n$ is insignificant. For $t_{gel}$, a paper by Aciero et al. (2002) also indicates that there is no influence. However, in the current study it has been demonstrated that $t_{gel}$ comparison for different samples is not straightforward, especially for samples with a broad molar mass distribution and very high $M_w$ like BR200. The crossover frequency $\omega_x$ for this sample is so low that it is not possible to determine a reliable value for $t_{gel}$. For PB0400 and PB0300, the $t_{gel}$ has been proven to be the same when the initial $tan \delta$ values are the same for both samples. Other methods to determine $t_{gel}$ should be adopted when a sample with low $\omega_x$ is concerned, or where the experiments are done at low temperatures. Aciero and Grizzuti (2003) suggested an “inverse-quenching” technique that can overcome this problem. This could be the next step in conducting a more comprehensive evaluation of how the gel time depends on various parameters.

Other molecular parameters such as isotacticity, presence of nucleants, and copolymer content were also considered in this quiescent crystallization study. It was found that a slight decrease in isotacticity brings about a reduction in the melting point, but does not affect the temperature dependence of quiescent crystallization kinetics (measured by the degree of undercooling). With the nucleants, the HDPE-type nucleant only affected the temperature dependence slightly and caused no change in either the melting point (compared to the non-nucleated BR200) or crystal morphology. On the other hand, the EBS-type nucleant caused a 2 $^\circ$C increase in melting point and about 20 times increase in quiescent crystallization kinetics, although with similar temperature dependence. Additionally, the crystals formed are much smaller compared to those in BR200 or BR200-X1. Significant effects on crystallization kinetics were also observed with the copolymers, which have much lower melting points compared to the homopolymers with similar molecular weights. The copolymers have different temperature dependences compared to each other and the homopolymers. This suggests another crystallization mechanism that generates crystals having more defects.
5. SHEAR-INDUCED CRYSTALLIZATION

In almost all polymer processing situations, the polymer melt crystallizes not in quiescent condition but under the influence of flow, which can accelerate the crystallization kinetics by orders of magnitude and induce dramatic changes in morphology. Consequently, the understanding of how flow affects crystallization is essential in analyzing the processing-structure-property relations. Flow-induced crystallization has been studied extensively during the last three decades – most, however, concentrates on one type of flow: shear flow, which is dominant in processes such as extrusion and injection molding. The relative ease with which pure, simple shear can be simulated contributes to the wide choice of experimental methods available (see Table 2.3). Empirical studies on shear-induced crystallization (SIC) usually adopts either continuous shear or step shear approach. Proponents of the step shear method (e.g. Liedauer et al. (1993), Vleeshouwers and Meijer (1996), and Kumaraswamy et al. (1999)) argue that to analyze the effect of shear on crystallization, the two occurrences must be carefully separated to avoid a complex interdependence (as the sample crystallizes, the flow properties are also inevitably modified).

In this study, continuous shear rate is applied in all experiments, i.e. the change in properties of the sample is monitored as the shear is applied and the sample crystallizes. This more closely resembles what happens in the real processing situations – for example, as the polymer melt is injected into a cool mold, the melt will crystallize under the influence of shear. Several examples that use continuous shear rate in their experiments are Lagasse and Maxwell (1976), Wassner and Maier (2000), and Acierno et al. (2003).

Despite significant research efforts, the picture on SIC is far from complete, especially if one considers the effects of various parameters, both from the flow and the intrinsic properties of the sample. Systematic experiments at high shear rate range are still lacking, in particular those concerning continuous shear rate. For example, in the experiments of Acierno et al. (2003), the maximum shear rate attempted is still below 10
s\(^{-1}\), whereas in injection molding, typical shear rates range from \(10^2 \text{ – } 10^4 \text{ s}^{-1}\) (Isayev et al., 1995).

This chapter aims to investigate the SIC behavior of PB-1, starting with one sample (PB0400) at relatively low shear rates. The dependence of crystallization onset time on the degree of undercooling and magnitude of shear rate is studied for this sample. In most cases, low to moderate undercooling was applied in order to allow a sufficient time window for observation. A scaling law that is able to describe the crystallization behavior of a sample and construct a temperature-invariant curve is proposed, using the quasi-quiescent onset time \(t_{on,q}\) as the normalizing parameter.

The next step is to study the influence of various molecular parameters on SIC, as has been done in Chapter 4 for quiescent crystallization. The significance of the temperature-invariant curve as a means to compare the SIC behavior is shown using three samples: PB0400, PB0300, and BR200. Finally, in this chapter two experimental methods are introduced, with which the range of shear rates can be extended up to 500 \(\text{s}^{-1}\). The experimental challenges and the agreement of results with those obtained from the conventional method (using rotational rheometer) are discussed.

5.1 SIC Behavior of PB0400

The dependence of crystallization onset time \(t_{on}\) on temperature was initially studied using PB0400 as the sample, because of practical reasons. This grade has a relatively low viscosity (permits higher shear rates to be imposed before the torque limit of the device is exceeded) and is also well-characterized (see Tables 3.3-3.7). The ARES rotational rheometer, as described in Chapter 3.2.1, was utilized, with shear rates ranging from \(10^{-4} \text{ – } 0.3 \text{ s}^{-1}\). Other conventions in the experiment, such as sample preparation, temperature protocol, and selection of \(t = 0\), are the same as explained in Chapter 4.1. The onset time was determined as illustrated in Figure 4.2, by taking the instant where the level of viscosity \(\eta(t)\) reaches twice the initial viscosity value \(\eta(0)\). The upper shear rate limit of 0.3 \(\text{s}^{-1}\) was chosen because at larger shear rates the sample was fractured and extruded out of the plates before reaching the desired level of viscosity.
5.1.1 Dependence of Crystallization Onset Time on Temperature

Figure 5.1 Normalized viscosity development curves for PB0400 at crystallization temperatures of 99 °C, 103 °C, and 107 °C, and shear rates from $10^{-4}$ up to 0.3 s$^{-1}$.

99 °C, 103 °C, and 107 °C, and shear rates from $10^{-4}$ up to 0.3 s$^{-1}$. 
In Figure 5.1, the normalized viscosity curves for PB0400 sheared at $10^{-4} - 0.3\ \text{s}^{-1}$ and at three temperatures ($99\ ^\circ\text{C}$, $103\ ^\circ\text{C}$, and $107\ ^\circ\text{C}$) are shown. The selection of the lower limit ($99\ ^\circ\text{C}$) is particularly important, because at low temperatures the onset time may become very small and significant crystallization in the sample may occur before a stable sample temperature is reached. Conversely, the temperature should not be too close to the melting point ($T_{m2}$ for PB0400 = $110.7\ ^\circ\text{C}$) because then the measurement will take too much time, especially considering the low shear rates.

The viscosity values in the graph have been normalized to the steady-state viscosity value $\eta_{SS}$. In most cases, $\eta_{SS}$ represents the constant viscosity achieved at the start of the experiment. However, at higher shear rates some form of instability may set in and a decreasing slope is seen at the start instead. In this case, $\eta_{SS}$ is defined as the plateau viscosity value after the slope and before it climbs up due to crystallization.

To test the reproducibility of the shearing experiment, several runs were repeated at $103\ ^\circ\text{C}$ for the maximum and minimum shear rates (i.e. $0.3\ \text{s}^{-1}$ and $10^{-4}\ \text{s}^{-1}$, respectively). This is shown in Figure 5.2, and it is clear that the reproducibility is very good. Variations in $t_{on}$ are less than 5 minutes, and an error estimate of 10% is given.

![Graph showing viscosity over time](image)

**Figure 5.2** Reproducibility runs for PB0400 at $103\ ^\circ\text{C}$, sheared at $0.3\ \text{s}^{-1}$ and $10^{-4}\ \text{s}^{-1}$.
The temperature of the sample is expected to be true and constant during the experiment, with an estimated error of less than 0.3 °C. The device has been calibrated carefully and at such low shear rates, it is unlikely that significant shear heating occurs.

Figure 5.3 plots the onset time vs. shear rate at the three temperatures, and Table 5.1 lists the numerical values of these onset times. At 107 °C, the quasi-quiescent onset time \( t_{on,q} \) reaches \( 10^5 \) s or almost 28 hours, although this temperature is still 4 °C lower from \( T_{m2} \) (110.7 °C). It can be imagined that to determine \( t_{on,q} \) even closer to \( T_{m2} \) the experiment time will be impractically long.

![Figure 5.3 PB0400 crystallization onset time at 99 °C-107 °C and a range of shear rates.](image)

<table>
<thead>
<tr>
<th>( t_{on} ) (s)</th>
<th>99 °C</th>
<th>103 °C</th>
<th>107 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001 s(^{-1})</td>
<td>5.58(\times)10(^3)</td>
<td>2.28(\times)10(^4)</td>
<td>1.02(\times)10(^5)</td>
</tr>
<tr>
<td>0.001 s(^{-1})</td>
<td>5.64(\times)10(^3)</td>
<td>2.55(\times)10(^4)</td>
<td>1.17(\times)10(^5)</td>
</tr>
<tr>
<td>0.01 s(^{-1})</td>
<td>5.82(\times)10(^3)</td>
<td>2.32(\times)10(^4)</td>
<td>4.93(\times)10(^4)</td>
</tr>
<tr>
<td>0.03 s(^{-1})</td>
<td>6.66(\times)10(^3)</td>
<td>1.58(\times)10(^4)</td>
<td>3.56(\times)10(^4)</td>
</tr>
<tr>
<td>0.0646 s(^{-1})</td>
<td>3.66(\times)10(^3)</td>
<td>8.46(\times)10(^3)</td>
<td>1.24(\times)10(^4)</td>
</tr>
<tr>
<td>0.139 s(^{-1})</td>
<td>1.92(\times)10(^3)</td>
<td>5.58(\times)10(^3)</td>
<td>6.18(\times)10(^3)</td>
</tr>
<tr>
<td>0.3 s(^{-1})</td>
<td>1.26(\times)10(^3)</td>
<td>2.58(\times)10(^3)</td>
<td>2.82(\times)10(^3)</td>
</tr>
</tbody>
</table>
The plateau-and-slope trend is evident for all temperatures, with the plateau region becoming shorter at higher temperatures. This is in accordance with the observation of Acierno et al. (2003), in which it is found that as temperature decreases, the contribution of flow as a driving force to crystallization also decreases. In other words, flow is more influential at high temperatures and it is easier for small flows to cause the transition from quasi-quiescent to flow-induced regions.

The plateau region is followed by a systematic decrease in onset times with increasing shear rates, similar to what has been found by Lagasse and Maxwell (1976) in their experiments with polyethylene. It is also apparent from Figure 5.3 that at higher shear rates, the difference between onset times at different temperatures becomes smaller. The slightly decreasing slopes as the temperature is reduced reinforce the statement in the previous paragraph, that flow becomes less effective in enhancing crystallization at lower temperatures (although the absolute value of the crystallization onset time might still be lower than at higher temperatures).

5.1.2 Temperature-Invariant Curve

As seen in Figure 5.3, shear flow and temperature contribute to crystallization onset time in different ways. Therefore, it would be useful to develop a normalization method that can create a temperature-invariant representation of the $t_{on}$ obtained for a sample. This representation is intended as a crystallization onset time “fingerprint” for the sample, and if successful, the measurements for other samples can be restricted to a few temperatures and/or shear rates.

As a first step to eliminate the temperature effect, the onset times are normalized with respect to $t_{on,q}$ at their respective temperatures. Although this means that several values of $t_{on,q}$ must first be obtained, once the exponential trend as seen in Figure 4.12 has been established, the $t_{on,q}$ values for the intermediate temperatures can simply be calculated. The result of this “first attempt” is shown in Figure 5.4. The error bars are given only for the 99 °C dataset to maintain clarity. It is clear that this step is not sufficient because the data points do not converge in the high shear rate range.
Hence, an additional horizontal shift is required. It was found that by multiplying the shear rate by $t_{on,q}^{0.5}$, the data points collapse on one curve within experimental accuracy (Figure 5.5). Changing the exponent does not improve the outcome significantly. Although the proposed normalization procedure has a purely phenomenological origin, it will be discussed in Section 5.1.4 that the idea agrees with former findings of Eder and Janeschitz-Kriegl (1997). One consequence of the normalization method is an awkward unit of s$^{-0.5}$ for the x-axis. An extra step by multiplying with an additional time constant gives a dimensionless number, the justification of which will be introduced in Section 5.1.3.
The curve in Figure 5.5 can be fitted with a three-parameter Cross function as given below:

$$t_{on} = \frac{t_{on,q}}{1 + (\beta \gamma^{0.5} t_{on,q})^c}, \quad (5.1)$$

with $\beta = 0.16 \, s^{0.5}$ and $c = 1.3$ for PB0400.

Equation 5.1 contains implicitly the dependence of quiescent onset time on the degree of undercooling, as given in Equation 4.7. Thus, a more general relationship between the onset time, temperature, and shear rate can be described as:

$$t_{on} = \frac{A \exp[B(T_m - T)]}{1 + C \gamma^m \exp[D(T_m - T)]}, \quad (5.2)$$

where the corresponding parameters for PB0400 are:

- $A = 5 \times 10^5 \, s$, $B = -0.35 \, K^{-1}$, $C = 467 \, s^{1.3}$, $D = -0.23 \, K^{-1}$, and $m = 1.3$.

5.1.3 Introduction of Characteristic Retardation Time

The enhancement in crystallization kinetics in the flow-induced region of Figure 5.5 is determined not only by the magnitude of flow, but also by the molecular parameters of the sample itself. It is therefore reasonable to introduce another factor to the normalization method, namely the characteristic retardation time $\tau$. As already mentioned in Chapter 4: Quiescent Crystallization, the characteristic retardation time...
is a measure of how quickly the oriented chains return to their random state after the external stress has been eliminated. The method to calculate $\Lambda$ is also given in Equations 4.4 and 4.5. It is different from the longest relaxation time $\tau$, which refers only to the long-chain portion of the sample. As will be seen later on, the significance of $\Lambda$ becomes clearer when the T-invariant curves from different samples are compared.

To balance the exponent at the x-axis and make the axis dimensionless, an additional multiplication by $\Lambda^{0.5}$ in the normalization procedure was selected. In one respect, the introduction of $\Lambda$ brings back the temperature dependence to the T-invariant curve. However, as is clear from Figure 4.12, this temperature dependence is much lower than that of onset time. Therefore, it is reasonable to say that the inclusion of $\Lambda$ does not significantly alter the T-invariant property of the curve. In Figure 5.6, the T-invariant curve is shown after the extra multiplication by $\Lambda$.

![Figure 5.6 The T-invariant curve for PB0400 after multiplication of the abscissa by $\Lambda^{0.5}$.](image)

5.1.4 Physical Background

The normalization procedure has so far been introduced based on empirical result, and although it is successful in combining the data points together, there is still the question of whether a relevant physical relationship exists. A similarity of the normalizing parameter for the T-invariant curve ($\dot{\gamma} t_{on,q}^{0.5}$) can be found in the analysis of Eder and
In their study, it is proposed that the number of nuclei $N$ in shear-induced crystallization is equal to the sum of quiescent nuclei $N_0$ and shear-induced nuclei $N_f$. The latter follows the differential equation:

$$
\dot{N}_f = (\dot{\gamma} / \dot{\gamma}_n)^2 g_n - N_f / \lambda_f ,
$$

(5.3)

where $\lambda_f$ stands for a relaxation time (which can be assumed to be infinite under a steady shear rate $\dot{\gamma}$), $\dot{\gamma}_n$ a characteristic shear rate, and $g_n$ a pre-factor with dimensions $\text{m}^{-3}\text{s}^{-1}$. Equation 5.3 is the same as Equation 2.9, with $\lambda_f$ replacing $\tau_n$ as the relaxation time). For a constant shear rate, this yields with $\lambda_f = \infty$:

$$
N = N_0 + \frac{g_n}{\dot{\gamma}_n^2} \dot{\gamma}^2 t
$$

(5.4)

In shear-induced crystallization, the small number of quiescent nuclei (being approximately constant vs. time) will finally be overruled by the number of shear-induced nuclei. Then, according to Equation 5.4, these shear-induced nuclei will increase proportionally to $\dot{\gamma}^2 t$. The first observation of a reduction of the onset time due to shear, however, will occur close to the quiescent onset time $t_{on,q}$. It is thus reasonable that a scaling with $\dot{\gamma}^2 t_{on,q}$ or $\dot{\gamma} t_{on,q}^{0.5}$ is found.

### 5.2 Extension into High Shear Rate Range

The SIC experiments using a conventional plate-plate setting in the ARES Rheometer can only access a limited range of shear rates, normally up to 1 s$^{-1}$ or 2 s$^{-1}$. Beyond this, the sample was usually thrown out of the plates before a substantial increase in viscosity could be observed, as can be seen in Figure 5.7. The problem is more evident for lower temperatures. This range is far below the shear rate range encountered in processing conditions, which ranges between $10^3$ s$^{-1} – 10^4$ s$^{-1}$ for extrusion and up to $10^5$ s$^{-1}$ for injection molding. Therefore, alternative methods have to be sought that are able to impose shear rates closer to processing conditions. In *step shear*, this challenge has been addressed by several researchers, for example Janeschitz-Kriegl et al. (1983), Duplay et al. (2000), and Kornfield et al. (2002). However, in *steady shear* a well-developed method is still lacking, and most of the experiments done in this area (e.g. Lagasse and

Figure 5.7 Examples of the drop in viscosity due to the sample being thrown off the plates in ARES experiments, using PB0400 at several temperatures.

5.2.1 Capillary Rheometer

The experimental procedure using the capillary rheometer and the schematic have been described in Section 3.2.2.2. The crystallization kinetics was monitored from the evolution of pressure, measured just before the die entrance with a pressure transducer. As the sample has to be melted first and then cooled before the experiment starts, there was a problem of sample shrinkage and the creation of air bubbles. To avoid this and to ensure that the piston stays in contact with the sample at the crystallization temperature, the sample was always pressurized to 10 bar at 180 °C. For this purpose, a mechanical plug was installed at the die outlet to prevent the sample coming out from the die.

Another, more important use of the mechanical plug is to impose an initial pressure $P_i$ at the crystallization temperature, just before the experiment was started. Such measure is necessary to have a stable pressure profile at the start, which would allow for an unambiguous determination of the onset time. The process is illustrated in Figure 5.8.
Figure 5.8 Schematic of the capillary rheometer during (a) pressurizing of sample and (b) extrusion. The initial pressure $P_i$ corresponds to the extrusion pressure at the undercooled temperature set in the experiment. Figure 5.9 shows an example of how $P_i$ is estimated at 107 °C. First, the flow curve of the sample at 160 °C is constructed by extruding the sample (PB0400) at this temperature and several shear rates (using the same die). The resulting viscosity function $\eta_{app}(\dot{\gamma}_{app})$ is then shifted to 107 °C using the Arrhenius shift factor $a_T$ (see Table 3.8 for the activation energy). Then, it was converted into a pressure function $P(\dot{\gamma}_{app})$ using the following relationship:

$$P = \frac{2}{R} \frac{L}{\eta_{app} \dot{\gamma}_{app}}$$  \hspace{1cm} (5.5)
If $P_i$ was not adequately chosen, there will be a pressure transient at the start of the experiment, which complicates the definition of a reliable $P_{SS}$. For example, if $P_i$ was too low, the piston would only compress the sample and not push it through the die at the start of the experiment. On the other hand, if $P_i$ was too high, there was a higher stress on the sample that acted as an extra driving force for crystallization. Equation 5.5 can be used without Bagley or Rabinowitsch-Weissenberg correction because the experiment was only concerned with the apparent viscosity.

The amount of pressure that the plug can withstand is limited to around 500 bar, above which leakage of sample occurs. However, this was already enough to achieve shear rates up to 1000 s$^{-1}$ at the temperatures used in the experiments. After the extrusion was started for some time, crystallization occurred and this could be seen from the increase in pressure signal. The crystallization onset time $t_{on}$ was chosen as the time when $P(t) = 2P_{SS}$, similar to the case with the ARES rotational rheometer. $P_{SS}$ is the steady-state pressure that should be evident at the start of the experiment.

The capillary rheometer was quite bulky and hence the cooling rate was very slow, around 2 °C min$^{-1}$, as compared to that in the ARES (15 °C min$^{-1}$). For this reason, the degree of undercooling could not be set too large, otherwise quiescent crystallization would set in before the experiment was started (the same problem is also present in the experiments using ARES, but here the temperature window was even more limited because of the lower cooling rate). The temperature control in the cylindrical die was achieved by inserting probes into two small holes on the side of the die, one at 3 mm from the top and the other at 3 mm from the bottom. The ends of the holes have a distance of 1 mm from the capillary. With this method, the sample temperature can be estimated within reasonable accuracy of ± 0.5 °C.

5.2.1.1 Experimental Results

In Figure 5.10, the results from the capillary rheometer experiments for PB0400 at 107 °C are shown. A wide range of shear rates (from 1 s$^{-1}$ – 500 s$^{-1}$) could be accessed without stability problems. The sharp upshoot in pressure is similar to the viscosity
upshoot in the ARES experiments, and it is clear from the graph that the onset time decreases as shear rate increases. At very large shear rates, however, the onset time may become very short (in this range of undercooling) that it is difficult to observe the plateau in viscosity. In this experimental setup, shear heating due to the high shear rates applied was less severe compared to that in the concentric cylinder rheometer (see Section 5.2.2), because the major part of the sample was extruded continuously through the die.

Figure 5.10 Results from capillary rheometer for PB0400 at 107 °C, various shear rates.

The reproducibility of the capillary rheometer experiments is very good, as long as the requirement of having a stable pressure profile at the start is fulfilled. Figure 5.11 shows that both for low and high shear rates, the scatter in onset time values is about 10%.

Figure 5.11 Reproducibility of results from capillary rheometer experiments.
5.2.1.2 **Visualization of Die Blocking Process**

The pressure increase in the die is caused by progressive blockage of the capillary by the crystallizing sample. To visualize how this blocking takes place, an experiment was conducted using the Multipass Rheometer (MPR) fitted with a slit die geometry. The MPR permits observation of the flowing sample through glass windows installed at opposite sides of the die. Figure 5.12 depicts the blocking process, which can be clearly seen to start at the wall near the outlet of the die and then progressing to the center of the die. The reason for this behavior is that the shear rate at the wall is the highest, and near the outlet of the die there is an expansion of flow, introducing some elongational flow component that increases the stress on the sample. The solidification at the wall reduces the effective radius of the die, which in turn leads to stronger shearing because the flow rate was kept constant.

![Images showing development of crystallization in a slit die](image)

*Figure 5.12 Development of crystallization in a slit die having length of 8 mm and thickness of 10 mm, for PB0400 extruded at 99 °C and 200 s⁻¹. Times shown are counted from the start of extrusion.*

5.2.2 **Concentric Cylinder Rheometer**

The second device used to perform crystallization experiments at high shear rates was the concentric cylinder rheometer, the schematic of which is already given in Figure 3.9. The sample was sheared in the chamber between the bob and the cup, and the torque as a function of time $M(t)$ was monitored. After a certain time, crystallization started and a sharp upshot in the torque signal was observed. In this case, the crystallization onset time $t_{on}$ was defined as the instant when $M(t) = 2M_{SS}$, with $M_{SS}$ being the stable torque level at initial stages of the experiment.
Similar to the capillary rheometer, the cooling rate that could be realized with this device was around 2-3 °C min\(^{-1}\). The sample temperature was estimated by inserting a temperature probe at the top cover, which has a cavity extending to 1 mm away from the base (i.e. very close to the chamber filled with sample). Because of the closed nature of the chamber, at high shear rates there was evidence of shear heating of the sample after a certain time. This is shown in Figure 5.13. Consequently, at high shear rates the onset time might become longer than expected due to the higher sample temperature.

![Figure 5.13](image)

**Figure 5.13** Transient torque and temperature signals in the concentric cylinder rheometer during shearing of BR200 at 107 °C and 30 s\(^{-1}\). Evidence of shear heating can be observed, where the dashed line indicates \(T = 107 °C\).

Results for the shear-induced crystallization experiments with PB0400 using the concentric cylinder rheometer are shown in Figure 5.14, while the reproducibility of the experiments is demonstrated in Figure 5.15. From the upshoot in torque signal, it is clear that as the shear rate increases, the onset time becomes faster. However, above a certain shear rate a drop in torque signal is observed after the upshot (see the curves for 50 s\(^{-1}\) and 100 s\(^{-1}\) in Figure 5.14), which may indicate fracture of the sample. In this range the effect of shear heating also becomes significant, therefore the applied shear rate range is limited to 5-100 s\(^{-1}\). The reproducibility of the runs is good, with an estimated scatter of 15%.
5.2.3 Comparison with ARES Results

The crystallization onset times for PB0400 from both methods are compared in Figure 5.16. As seen previously from the ARES results (Figure 5.3), as the shear rate increases the onset time becomes less sensitive to temperature, compared to the low shear rate or quiescent region. At 107 °C, a significant gap is observed between the onset times from the concentric cylinder and capillary methods at the same shear rates.
Figure 5.16  Onset time data obtained from concentric cylinder and capillary rheometers for PB0400. In Figure 5.17, a comparison is given for the signals used to monitor crystallization progress: viscosity for ARES, pressure for capillary rheometer, and torque for concentric cylinder rheometer. The example refers to an experiment run with PB0400 at 112 °C and 5 s⁻¹. It is important to note that the shear rate of 5 s⁻¹ here refers to the rim shear rate in ARES, the true shear rate in the concentric cylinder device, and the apparent wall shear rate in the capillary rheometer. A relatively high temperature of 112 °C (slightly above $T_{m2}$ for PB0400) was chosen for this particular example so that a high shear rate could be applied while keeping the crystallization time at a moderate level.

Figure 5.17  Comparison of output signals during SIC experiments for PB0400 at 112 °C and 5 s⁻¹ using three experimental methods (ARES, capillary rheometer, and concentric cylinder rheometer).
It is clear from Figure 5.17 that the pressure signal from the capillary rheometer climbs somewhat later compared to the torque and viscosity signals. This can be attributed to the different flow situation encountered in the cylindrical die compared to those in the other two devices. In the capillary die, a fresh sample from the reservoir is extruded continuously, whereas in the concentric cylinder and ARES, the same sample element stays inside the chamber or between the plates while being sheared.

The onset times obtained from the three methods at shear rates ranging from $10^{-4}$ to 500 s$^{-1}$ and temperatures 99 – 107 °C are summarized in Figure 5.18, in the form of T-invariant curves like in Figure 5.5. It should be emphasized again that the x-axis in Figure 5.18 uses $\dot{\gamma} * t_{on,q}^{0.5}$ instead of $\dot{\gamma}$. By addition of data points from the concentric cylinder rheometer to the ARES data, an extension of the curve up to 100 s$^{-1}$ is possible.

At this maximum shear rate, some deviations to longer onset times than expected are observed, which are most likely due to effects of shear heating. Although an offset is present for the onset times from capillary rheometer, the slope for these data points is the same as for the main curve (-1), suggesting a possibility of another shift factor. By adding the capillary rheometer results, the shear rate can be extended further to 500 s$^{-1}$.

Figure 5.18  Temperature-invariant curve for PB0400, combining the onset time data from ARES ($10^{-4} – 2$ s$^{-1}$), concentric cylinder rheometer (5 – 100 s$^{-1}$), and capillary rheometer (1 – 500 s$^{-1}$), for $T = 99 – 107$ °C.
The T-invariant curve can be fitted with a Cross function, just like in Equation 5.1, with the following parameters:

$$\beta = 0.3 \ s^{0.5}, \ c = 1.$$ 

These values are slightly different to the values originally estimated only with the onset times at low shear rates ($\beta = 0.16 \ s^{0.5}, \ c = 1.3$). However, the fit obtained using a wider range of shear rate is more reliable, and the error is estimated to be less than 15%.

### 5.3 Effect of Molecular Weight Distribution

To investigate the effect of molecular weight distribution on shear-induced crystallization, the same three samples as chosen for the quiescent crystallization study (refer to Chapter 4.4.1) were used, namely PB0400, PB0300, and BR200. The relevant properties for these samples are listed in Tables 3.3-3.7, but for clarity, Table 5.2 below contains a summary of these properties. The mastercurves of viscoelastic properties (reference temperature = 150 °C) are also shown in Figure 5.19 (a)-(c) (see Appendix E for the complete list of mastercurves).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kD)</th>
<th>$M_w$ (kD)</th>
<th>$M_z$ (kD)</th>
<th>$M_w/M_n$</th>
<th>$M_z/M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0400</td>
<td>31</td>
<td>176</td>
<td>368</td>
<td>5.7</td>
<td>2.1</td>
</tr>
<tr>
<td>PB0300</td>
<td>35</td>
<td>305</td>
<td>744</td>
<td>8.7</td>
<td>2.4</td>
</tr>
<tr>
<td>BR200</td>
<td>39</td>
<td>762</td>
<td>2 460</td>
<td>19.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$G'_x = G''_x$ (kPa)</th>
<th>$\omega_c$ (rad/s)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$J'_c^0$ (Pa^{-1})</th>
<th>$E_a$ (kJ/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0400</td>
<td>24</td>
<td>70</td>
<td>1800</td>
<td>1.64 x 10^{-4}</td>
<td>49</td>
</tr>
<tr>
<td>PB0300</td>
<td>18</td>
<td>9.9</td>
<td>11 000</td>
<td>2.27 x 10^{-4}</td>
<td>49</td>
</tr>
<tr>
<td>BR200</td>
<td>9.4</td>
<td>0.32</td>
<td>230 000</td>
<td>4.28 x 10^{-4}</td>
<td>48</td>
</tr>
</tbody>
</table>

From the table and the graphs, it is clear that the crossover frequency becomes smaller in magnitude while the zero-shear viscosity increases in decades as one moves from PB0400 to BR200. The first trend reflects the broadening in molecular weight distribution, while the second indicates the significant increase in $M_w$.  

103
(a) Moduli $G', G''$ (Pa)

Angular Frequency $\omega.a_T$ (rad/s)

Complex Viscosity $\eta^*$ (Pa.s) 

$T_{ref} = 150 \, ^\circ C$

(b) Moduli $G', G''$ (Pa)

Angular Frequency $\omega.a_T$ (rad/s)

Complex Viscosity $\eta^*$ (Pa.s) 

$T_{ref} = 150 \, ^\circ C$
Figure 5.19  Master curve of viscoelastic properties of (a) PB0400, (b) PB0300, and (c) BR200 at $T_{ref} = 150 \, ^\circ C$. Individual curves were obtained at 130 °C, 150 °C, 170 °C, and 190 °C.

The same shearing experiments with ARES (i.e. low shear rates) as those done for PB0400 were conducted for PB0300 and BR200. The crystallization onset times, $t_{on}$, are shown in Figure 5.20 (a)-(b). Because a T-invariant curve can now be constructed, a fewer number of measurements for these samples were necessary. Therefore, only two temperatures were tested here. For BR200, it was safer to choose 107 °C instead of 99 °C to avoid quiescent crystallization before the experiment starts, because the crystallization kinetics of this sample is faster compared to the other two.
Figure 5.20 Dependence of onset time on temperature and shear rate for (a) PB0300 and (b) BR200.

For PB0300, the plateau and slope regions can be clearly seen, and the critical shear rate where $t_{on}$ starts to decrease is similar to PB0400, around 0.1 s$^{-1}$. For BR200, the plateau region cannot be clearly identified in Figure 5.20(b). There is only a marked change of slope between the range from $10^{-4}$ s$^{-1}$ to $10^{-2}$ s$^{-1}$ and from $10^{-2}$ s$^{-1}$ upwards. However, by performing a creep experiment on BR200 a lower shear rate than $10^{-4}$ s$^{-1}$ can be accessed to test if a quasi-quiescent condition has been reached. For samples with high molecular weight, the creep test is particularly useful for this purpose, as already discussed in
Chapter 4.2.4. In Figure 5.21, a constant stress of 10 Pa was used, which translates into a shear rate of $10^5$ s$^{-1}$, considering the viscosity of the sample at the temperature of the experiment ($10^6$ Pa.s at 103 °C). Apparently, the crystallization onset time at this condition is 8500 s, close to the value obtained in the ARES at $10^{-4}$ s$^{-1}$ (9000 s). Therefore, this confirms that $10^{-4}$ s$^{-1}$ is small enough to reach the quasi-quiescent condition.

Figure 5.21 Creep experiment result for BR200 at $T = 103$ °C, using a constant stress $\tau = 10$ Pa. The graph is drawn on a semi-log scale.

5.3.1 Temperature-Invariant Representation

The T-invariant representations of the three samples are given in Figure 5.22. Each symbol refers to a sample and the experimental data points were obtained at temperatures ranging from 99 °C – 107 °C. The lines are the Cross model fits for each curve, the parameters of which are listed in Table 5.3. All the three curves have a similar shape. As the molecular weight increases, the curve is shifted to the left, indicating faster crystallization kinetics. For BR200, it is also apparent that the transition region between the plateau and slope is very broad, which means that the sample is very sensitive even to weak flows. This reflects its broad molecular weight distribution, in which the longest chains are readily oriented by flow and act as the trigger for further crystallization involving the shorter chains.
Table 5.3 Cross fit parameters (from Equation 5.1) for the T-invariant curves of PB0400, PB0300, and BR200.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0400</td>
<td>0.14</td>
<td>1.3</td>
</tr>
<tr>
<td>PB0300</td>
<td>0.22</td>
<td>1.3</td>
</tr>
<tr>
<td>BR200</td>
<td>1.1</td>
<td>1</td>
</tr>
</tbody>
</table>

In Figure 5.22, only the data points obtained by ARES (i.e. in the low shear rate region) are included. If the results from concentric cylinder rheometer experiments are added, the high shear rate region will appear as in Figure 5.23. Including these data points, the slopes of the PB0400 and PB0300 curves changed slightly and now all three curves have a common slope of approximately -1. This suggests the existence of a critical parameter that must be reached for shear-induced crystallization to occur. In this case, the governing parameter is $\gamma^{0.5} \times t_{on,q} / t_{on,q}$, or equal to $\gamma / t_{on,q}^{0.5}$ (the total strain divided by the root of quiescent onset time). The average values of $\gamma / t_{on,q}^{0.5}$ are 3.6 for PB0400 (neglecting the points suspected to be affected by shear heating), 2.2 for PB0300, and 0.9 for BR200.
The characteristic retardation time $\Lambda$, introduced in Chapter 4 and Figure 4.12, gains importance here because the three samples differ significantly in their breadth of the MWD, from which the value of $\Lambda$ is determined. The relative positions of the T-invariant curves change by using $\Lambda^{0.5}$ as an additional factor in the abscissa, as seen in Figure 5.24. As a result, the plateau to slope transition for all three curves coincides at one point, indicating that the onset of shear-induced crystallization is controlled by $\Lambda$. This is reasonable, because $\Lambda$ depends on the length distribution of the polymer chains, which in turn determines how sensitive the sample is to shear flow. However, after this transition point the data diverge a little because the influence of shear dominates. Other options of characteristic time are available to scale the experiments, such as the reptation time or retraction time, as mentioned in van Meerveld et al. (2004) in their rheological classification of FIC of polymer melts. Although $\Lambda$ might be a crude approximation of the molecular dynamics, its determination is more straightforward and practical for the purpose of this study.
5.3.2 Morphology

Several shearing experiments using the Linkam Cell were conducted for PB0400 and BR200. By this method it can be observed how the shearing conditions and molecular properties of the sample influence the resulting crystal morphology. In Figures 5.25(a) and (b) two shear rates were tested for BR 200. The higher shear rate (1 s\(^{-1}\)) produced a mixture of rod-like nuclei and spherulites, while the lower one (0.139 s\(^{-1}\)), although imposed for a longer time, only produced spherulitic structures. In both cases, shearing was stopped before the crystallites became visible, because if shearing is continued, the stress became too large and the sample will be damaged. Therefore, the Linkam Cell experiments were done in a step-shear mode, different to the experiments with the other devices so far, which employed the continuous-shear mode.
Figure 5.25 Morphology development of BR200 at 103 °C after subjected to: (a) shear of 0.139 s⁻¹ for 420 s, (b) shear of 1 s⁻¹ for 100 s. The times shown include shearing time. Flow direction is clockwise.
Figure 5.26 Morphology development of:
(a) PB0400 at 99 °C, sheared at 1 s$^{-1}$ for 150 s,
(b) BR200 at 99 °C, sheared at 1 s$^{-1}$ for 100 s.
Time scale includes shearing time. Flow direction is clockwise.
In Figures 5.26(a) and (b), similar shearing conditions at 1 s⁻¹ are compared for PB0400 and BR200. For PB0400, no rod-like structures were observed at all, while for BR200 almost all of the resulting crystallites are rod-like under this shearing condition.

The Linkam Cell results show agreement with the paper by Acierno et al. (2003), where it was proposed that the appearance of rod-like nuclei depends on a critical Deborah number \( De \), the product of shear rate \( \dot{\gamma} \) and longest relaxation time \( \tau_{max} \). For several grades of PB-1 used in their experiment, the critical Deborah number is estimated to be constant, around 160. In the current work, the characteristic retardation time \( \Lambda \) instead of \( \tau_{max} \) is used to describe the melt dynamics, since \( \Lambda \) is easier to estimate (see Equation 4.4) and also reflects the entire relaxation spectra of the sample, compared to \( \tau_{max} \), which refers mainly to the longest chains. The inability of PB0400 to produce rod-like nuclei at low shear rates becomes reasonable when one considers that its characteristic retardation time is two orders of magnitude lower than that for BR200 at the same temperature.

Table 5.4 summarizes the results from the Linkam Cell shearing experiments. Based on the data it can be estimated that the critical \( De \) for the transition between spherulitic and rod-like structures is 200. This means that for PB0400, one needs a shear rate of around 100 s⁻¹ to induce the rod-like morphology. Although a different characteristic time is used (\( \Lambda \) vs. \( \tau_{max} \)), the ballpark for \( De_{crit} \) agrees with what was proposed by Acierno et al. (2003) (\( De_{crit} = 160 \)). In their experiments, they did not investigate the effect of different shearing times on the morphology, but it has been established from other studies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature ( T(°C) )</th>
<th>Shear Rate ( \dot{\gamma} (s^{-1}) )</th>
<th>Characteristic Retardation Time ( \Lambda (s) )</th>
<th>Deborah Number ( De )</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB0400</td>
<td>99</td>
<td>1</td>
<td>2.2</td>
<td>2.2</td>
<td>Spherulitic</td>
</tr>
<tr>
<td>BR200</td>
<td>99</td>
<td>1</td>
<td>240</td>
<td>240</td>
<td>Rod-like</td>
</tr>
<tr>
<td>BR200</td>
<td>103</td>
<td>1</td>
<td>200</td>
<td>200</td>
<td>Spherulitic + Rod-like</td>
</tr>
<tr>
<td>BR200</td>
<td>103</td>
<td>0.14</td>
<td>200</td>
<td>28</td>
<td>Spherulitic</td>
</tr>
</tbody>
</table>
(Vleeshouwers and Meijer (1996), Devaux et al. (2004)) that shear rate is the more effective parameter compared to shearing time in SIC. With regards to the T-invariant curve, its validity seems unaffected by the crystallite morphology, as evident from Figure 5.22 that the T-invariant curve can also be constructed for BR200, up to the region where rod-like nuclei are expected.

5.3.3 Crystallization above $T_{m2}$

So far in this study, the crystallization experiments have been conducted below the melting point ($T_{m2}$). Actually, it is interesting to also investigate shear-induced crystallization above $T_{m2}$. In this region, there is no thermodynamic driving force. Hence, a sufficiently high shear is required to surpass the kinetic energy barrier towards crystallization. However, above a certain limit the continuous shearing will also break the formed crystals, and the effects of shear heating will also become more pronounced. It is reasonable, then, to expect a temperature region above $T_{m2}$ where crystallization occurs only in a certain shear rate range – which suggests that a “phase diagram” can be constructed.

For crystallization experiments above $T_{m2}$, the Couette-type device and capillary rheometer were used. The main aim here is to see whether crystallization occurs or not, rather than to measure the onset time. In any case, normalization with respect to quiescent onset time is not possible since above $T_{m2}$ there is no quiescent crystallization. Figures 5.27(a) - (c) show crystallization diagrams for PB0400, PB0300, and BR200, where the temperature is plotted against Deborah number. A maximum shearing time of 1 hour was imposed to see if the sample crystallizes. In this case, $De$ is an appropriate parameter since it takes into account the ability of the polymer chains to relax at a certain temperature. On the right side, the DSC curve for the second heating run $T_{m2}$ for each sample is included.

From the graphs, it is evident that the temperature limit where crystallization can occur above $T_{m2}$ differs significantly for the three samples, even though their melting points are quite close to each other. For BR200, SIC is still observed at 133 °C, which is 20 °C
above $T_{m2}$. On the other hand, for PB0400, the threshold seems to be only 3-4 °C above $T_{m2}$. Although, $T_{m2}$ is defined here as the peak temperature and therefore quiescent crystallization may be possible at temperatures between $T_{m2,peak}$ and $T_{m2,end}$, the graphs still clearly emphasize the role of long chains in inducing crystallization.
Although the influence of long chains has been demonstrated in this study, a clear quantification on the effects of molecular weight and molecular weight distribution in the high shear rate region is still missing. This would be a topic for further study, provided that well-defined samples are available. It would also be interesting to develop auxiliary units for the devices used in this study to enable morphological investigation, e.g. with X-ray or light scattering, so that the structure build-up (and at some point break-up) during continuous strong shear can be observed.

5.4 Effect of Isotacticity

In Chapter 4.4.2, quiescent crystallization experiments were done for two samples having different isotacticities: BR200 and PB0110M. SIC experiments using ARES were also conducted for these samples in the shear rate range of 0.0001 – 0.03 s\(^{-1}\), and the resulting viscosity curves are shown in Figures 5.28(a) and (b):
Figure 5.28 Viscosity curves for (a) BR200, and (b) PB0110M, showing shear-induced crystallization at 107 °C and several shear rates.

Using the ARES, the shearing experiments could run only up to 0.03 s\(^{-1}\) because the two samples have very high moduli, and the maximum torque was reached. Experiments with capillary rheometer are also problematic, because the sample is compressed inside the die instead of being extruded, which results in a steep climb of pressure from the start and later one cannot separate this effect from the increase of pressure due to crystallization. However, even in this small shear rate range the difference in SIC
behavior can be readily seen. In Figure 5.29, a plot of onset time against shear rate is shown, with an estimated error of 10%.

![Figure 5.29 Variation of crystallization onset time with shear rate for BR200 and PB0110M.](image)

It is already covered in Chapter 4.4.2 that in quiescent condition, the crystallization onset time of BR200 is three times longer than that of PB0110M due to the difference in melting points, which in turn is caused by the difference in isotacticity. As the shear rate is increased, the onset time for BR200 decreases more sharply compared to PB0110M until at 0.03 s\(^{-1}\) the onset times from the two samples are very close to each other. This is due to the effect of more long chains contained by BR200, which are “activated” to enhance the crystallization process once the shear rate is large enough. The more long chains that exist, the smaller this critical shear rate becomes. PB0110M, with a narrower distribution, does not exhibit such a drastic transition from quiescent to shear-induced crystallization onset times. In this case, the plateau is observed up to 10\(^{-3}\) s\(^{-1}\) (at 10\(^{-4}\) s\(^{-1}\), it is peculiar that the onset time is shorter than that at 10\(^{-3}\) s\(^{-1}\), but the variation still falls within experimental error). At larger shear rates and ultimately for shear rates close to processing conditions, it is expected that BR200 and PB0110M will behave in the same way in terms of their crystallization behavior. Therefore, in SIC, the molecular weight distribution (in particular the amount of long chains) plays a larger role than the isotacticity.
5.5 Effect of Nucleants

Figures 5.30(a) and (b) show the viscosity curves from SIC experiments performed on two nucleated versions of BR200, BR200-X1 and BR200-X2, at 107 °C. The two samples contain HDPE and EBS nucleating agents, respectively, in the same amount of 1000 ppm. The results for quiescent crystallization experiments are already covered in Chapter 4.4.3.

Figure 5.30  SIC viscosity curves for (a) BR200-X1 and (b) BR200-X2, at 107 °C and several shear rates.
The experiments were also done at 103 °C, and for BR200-X2, at 99 °C. Comparing the resulting crystallization onset times with those of BR200, Figure 5.31 is obtained.

From Figure 5.31, it is clear that also in shear-induced crystallization the HDPE nucleants do not have much effect on the onset time, compared with pure BR200. On the other hand, a substantial onset time reduction is seen for the EBS-nucleated sample, but this onset time tends to stay constant as the shear rate is increased. This indicates that the presence of EBS nucleants diminishes the contribution of the polymer chain length to the crystallization kinetics, because for the other samples a gradual reduction in onset time is observed as shear rate is increased, owing to better orientation of the polymer chains. Below 0.01 s⁻¹, the EBS-nucleated sample shows a flat plateau, indicating the quiescent region, compared to the slightly increasing slope for the other two samples.

In Chapter 5.1.2, the construction of a temperature-invariant curve was introduced for PB0400, containing the onset times at various shear rates and temperatures for one sample. The validity of this T-invariant curve has also been tested for BR200. In Figure 5.32, such curves are shown for BR200 and its two nucleated variants. For BR200 and BR200-X1, the T-invariant curves superimpose on each other, but that of BR200-X2 is located slightly to the right. This would confirm the point stated above, that the influence
of the polymer chains in BR200-X2 on shear-induced crystallization is somehow delayed by the presence of the EBS-nucleants. All three T-invariant curves have the same slope, however, which indicates that there is a same gain in crystallization kinetics from the imposition of shear flow.

![Normalized Onset Time vs. Normalized Shear Rate](image)

**Figure 5.32** Normalized onset time data for BR200, BR200-X1, and BR200-X2, taken at 103 °C and 107 °C.

In Figure 5.33, the development of crystallites after/during shear is shown. The sample is sheared at 99 °C for 100 s, with a shear rate of 1 s⁻¹. For BR200 and BR200-X1, no observable structure can be seen during shearing, but they develop soon afterwards. A mixture of rod-like structures and spherulites (in the case of BR200, mainly rod-like structures) is produced under this condition. The conditions required to induce the transition from spherulitic to rod-like structure are already discussed in Section 5.3.2, concerning the critical Deborah number. For BR200-X2, crystallites start to be observable even during shearing, and by the end of shearing (100 s) the area is already full of crystals. However, rod-like structures are not observed here. This would support the earlier suggestion that the nucleants “overshadow” the effectiveness of the molecular weight distribution in shear-induced crystallization.
Figure 5.33  Development of crystallites at 99 °C with shearing of 1 s$^{-1}$ for 100 s, for (a) BR200, (b) BR200-X1, and (c) BR200-X2. The time refers to time after shear is stopped ($t = 0$), except for BR200-X2.
5.6 Effect of Copolymer Content

The influence of copolymer content on SIC behavior was also investigated in this study, using the same two samples as with the quiescent crystallization experiments in **Chapter 4.4.4** (DP8010 and DP8310). The results are compared with the SIC behavior of BR200 and PB0300, respectively, which have similar molecular weight distributions with the copolymer samples, as can be seen in Figure 5.34 below.

![Figure 5.34 GPC curves of the C2C4 copolymers, BR200, and PB0300.](image)

Figures 5.35(a) and (b) show the array of onset times for DP8010 and DP8310, respectively, for a shear rate range of $10^{-4} - 0.1 \, \text{s}^{-1}$, with an approximate scatter of 10% for the data points. As with the other samples, a plateau-and-slope trend was observed here, with the critical shear rate of 0.001 $\text{s}^{-1}$ for DP8010 and 0.01 $\text{s}^{-1}$ for DP8310.
A T-invariant curve can be constructed from the onset time data following the method outlined previously. It was shown in Section 5.3.1 (see Figure 5.22) that for PB-1 homopolymers the T-invariant curves have a common slope of –1, although the slope is shifted to the left as $M_w$ increases (and $M_w/M_n$ becomes broader). In Figures 5.36(a) and (b), the results for the C2C4 samples are shown alongside those for PB0300 and BR200.
Figure 5.36 The normalized data points and T-invariant curves for (a) DP8010 and BR200, and (b) DP8310 and PB0300. The error bars for BR200 and PB0300 have been omitted to increase clarity.

Fitting the data points with a Cross function as given below, the values of $\beta$ and $c$ for the four samples are listed in Table 5.5.

\[
t_{on} = \frac{t_{on,q}}{1 + (\beta \cdot \dot{\gamma} \cdot t_{on,q}^{0.5})^c}
\]
Table 5.5 Cross fit parameters for the T-invariant curves of the four samples.

<table>
<thead>
<tr>
<th></th>
<th>DP8010</th>
<th>BR200</th>
<th>DP8310</th>
<th>PB0300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>1.1</td>
<td>1.1</td>
<td>0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>$c$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

From Figures 5.35 and 5.36 and from previous observations in Chapter 4.4.4, it can be concluded that the co-monomer units (at this concentration of 5.5%) has the largest effect on reducing the melting point (by 20-30 °C) and altering the mechanism of quiescent crystallization by producing, presumably, less perfect crystals. In shear-induced crystallization region, the difference between homopolymer and copolymer samples is apparent only for the low molecular weight samples at small shear rates, in which case the enhancement of crystallization kinetics from shear is reduced. At high shear rates, the T-invariant curves for PB0300 and DP8310 both show a slope of around -1, indicating the same gain in crystallization kinetics from shear. For the high molecular weight samples, no difference in shear-induced crystallization is observable even at low shear rates. These facts suggest that the long chains have a greater role than co-monomer content in shear-induced crystallization.
6. ELONGATION-INDUCED CRYSTALLIZATION

In polymer processing, elongational flow is particularly dominant for e.g. fibre spinning, film extrusion, and blow moulding. Literature and experimental data on elongation-induced crystallization (EIC) are still relatively scant compared to studies on shear-induced crystallization (SIC). It is already well-known for decades that elongational flow is more effective in enhancing crystallization than simple shear flow, compared at the same magnitude of deformation rate. Elongation is capable to create a larger degree of molecular orientation and stretching of the polymer chains. In this chapter, the elongation-induced crystallization behavior of PB-1 (only the uniaxial elongation is considered here) is investigated using a relatively new device (the Extensional Viscosity Fixture or EVF). A high molecular weight Polybutene-1 (PB-1) sample, BR200, is used here (the relevant properties can be seen in Table 6.1). The results are then directly compared with those obtained for the case of simple shear.

While a variety of well-established techniques to investigate shear-induced crystallization exists, the major challenge in elongation-induced crystallization has always been to find an appropriate technique, which combines uniaxial elongation with the possibility to impose a well-defined temperature protocol.

On-line observations of melt-spinning were pioneered by Ziabicki (1967), Nakamura et al. (1972), Spruiell and White (1975), Ishizuka and Koyama (1977), and Laun and Schuch (1989). With such methods, although flow rates as encountered in real process is achieved, it is difficult to separate the influences of flow and temperature because the process is non-isothermal. Elongational rheometers by Münstedt (1979) or Meissner (1969) solved this problem, but still they are less well-equipped for crystallization studies due to their bulky mass and therefore low cooling rates. Modified versions introduced by Kotaka et al. (1997) and Maia et al. (1999) have hardly been used to investigate elongation-induced crystallization. Stadlbauer (2004a, 2004b) developed the Windbix elongational rheometer and conducted elongation flow-induced crystallization experiments with short-term stretching, from which it was found that even a small amount of work is already enough to result in a significant multiplication of nuclei.
Okamoto et al. (1998a, 1998b) applied continuous stretching and performed a systematic approach concerning the influence of temperature and strain rate.

Strong extensional flows may be created by stagnation flows, like in the four-roll mill (Crowley et al. (1976), Dunlap and Leal (1987), McHugh et al. (1993)), opposed jets device (Mackay et al. (1995), Keller and Kolnaar (1997), Janeschitz-Kriegl et al. (2001)), and cross-slot device (Miles and Keller (1980), Gardner et al. (1982), Swartjes et al. (2003)). Swartjes et al. (2003) performed a comprehensive analysis based on birefringence and WAXS data obtained from the flow cell experiments, and simulated the results using Leonov and Pompon models. However, in this type of experiment shear gradients also exist close to the observation windows and influence the results.

Recently, an extensional tool consisting of dual wind-up drums was introduced by Sentmanat (2004). Another version of an extensional tool was developed by TA Instruments and commercialized as the Extensional Viscosity Fixture (EVF). The latter version is used here, which can be installed as an add-on tool in the ARES rotational rheometer. Accurate temperature control and fast cooling/heating rates achievable in the ARES are therefore retained, at least in principle. Another advantage is the upright arrangement of the sample strip, which reduces sagging. The small sample size also improves temperature homogeneity.

6.1. Experimental Methods

Table 6.1 summarizes the relevant properties of BR200, a high molecular weight isotactic PB-1 sample, which has also been used for the quiescent and shear-induced crystallization experiments.

<table>
<thead>
<tr>
<th>Isotactic PB-1 sample BR200</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight average molecular weight ($M_w$)</td>
<td>762 kg/mol</td>
</tr>
<tr>
<td>Number average molecular weight ($M_n$)</td>
<td>39 kg/mol</td>
</tr>
</tbody>
</table>

Table 6.1. Physical properties of BR200. 1st heating run refers to the as-received sample, whereas 2nd heating run refers to the reheating after the sample has been melted at 200 °C and cooled down to 25 °C (DSC cooling/heating rate was 20 K/min).
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>z-average molecular weight ($M_z$)</td>
<td>2 460 kg/mol</td>
</tr>
<tr>
<td>$M_w / M_n$</td>
<td>19.6</td>
</tr>
<tr>
<td>$M_z / M_w$</td>
<td>3.2</td>
</tr>
<tr>
<td>Isotacticity ($mmmm%$)*</td>
<td>90</td>
</tr>
<tr>
<td>Flow activation energy ($E_a$), $T_{ref} = 150 , \text{°C}$</td>
<td>48 kJ/mol</td>
</tr>
<tr>
<td>Zero-shear viscosity ($\eta_0$), $T = 150 , \text{°C}$</td>
<td>230 000 Pa.s</td>
</tr>
<tr>
<td>Melting point, 1$^{st}$ heating run ($T_{m1}$)</td>
<td>123.5 °C</td>
</tr>
<tr>
<td>Heat of fusion, 1$^{st}$ heating run ($\Delta H_1$)</td>
<td>62.6 J/g</td>
</tr>
<tr>
<td>Melting point, 2$^{nd}$ heating run ($T_{m2}$)</td>
<td>111.6 °C</td>
</tr>
<tr>
<td>Heat of fusion, 2$^{nd}$ heating run ($\Delta H_2$)</td>
<td>39.3 J/g</td>
</tr>
<tr>
<td>Crystallization point ($T_K$)</td>
<td>61.9 °C</td>
</tr>
<tr>
<td>Heat of crystallization ($\Delta H_K$)</td>
<td>31.0 J/g</td>
</tr>
</tbody>
</table>

### 6.1.1. Elongational Flow Set-up

The Extensional Viscosity Fixture (EVF) from TA Instruments consists of two vertical cylinders arranged in parallel, between which a sample strip having dimensions of 18 mm x 10 mm x 1 mm is positioned at middle height using two clips. A schematic is shown in Figure 6.1. The EVF is attached to the ARES rotational rheometer, with one cylinder connected to the force transducer, and the other to the motor. The outer cylinder revolves around the inner one while rotating on its own axis, thereby stretching the sample uniaxially. A constant Hencky strain rate was applied for each experimental run by applying constant rotational speeds. Because the movement is limited to one full revolution, the maximum Hencky strain achievable in this device is limited to $\varepsilon = 4.9$ for a sample thickness of 0.7 mm. Practically, the maximum Hencky strain that could be achieved in the experiments was about 3.5 because the sample thickness is about 1 mm and the sample on the drums comes in contact with itself before reaching one full revolution.

* NMR measurements by Basell Polyolefines in Ferrara, Italy.
Figure 6.1. Schematic of the Extensional Viscosity Fixture (EVF).

The temperature is regulated by blowing N\textsubscript{2} gas into the chamber (forced convection). A temperature sensor, which acts as a feedback for the temperature controller, is located close to the inlet of the N\textsubscript{2} gas. This location is 10 cm away from the centre of the sample. A temperature sensor closer to the sample, like that normally used for shear set-up in plate-plate or cone-plate geometry, is not available. Therefore, it is important to note that there is a distinct discrepancy between the chamber temperature (\(T_{\text{chamber}}\)) detected by the sensor and the actual sample temperature (\(T_{\text{sample}}\)). In steady-state condition, \(T_{\text{sample}}\) is always lower than \(T_{\text{chamber}}\), because there is a continuous heat loss through the shafts which are connected to the drive and transducer, remaining close to room temperature.

6.1.2. Calibration of the True Sample Temperature

Thus, calibrations had to be performed to determine \(T_{\text{sample}}\) both at the annealing temperature and in the undercooled states used for the EIC experiments. A solid Teflon (PTFE) strip with dimensions of 18 mm x 10 mm x 2 mm was cut and a hole with a diameter of 0.5 mm was drilled in the middle. A NiCr-Ni external thermocouple probe was placed inside this hole and the remaining space filled with silicone oil. This enabled
the detection of the temperature at the centre part of the sample, which is most relevant for the stretching experiments to be performed later. The heat conductivity of PTFE (0.23 W/m*K) is similar to that of PB-1 (0.22 W/m*K) (Saechtling, 1995), but PTFE does not melt at 180 °C - the nominal annealing temperature chosen for the experiments. The thickness of the PTFE sample (2 mm) is twice that of BR200 (1 mm). This is good, because it means that the equilibration time for BR200 sample will be shorter than the

Figure 6.2. Time dependence of $T_{chamber}$ and $T_{sample}$ for a PTFE sample with 2 mm thickness, during (a) heating from $T_{chamber} = 25 °C$ to $T_{chamber} = 180 °C$ at maximum heating rate, and (b) cooling from $T_{chamber} = 180 °C$ to $T_{chamber} = 107 °C$ at 15 K/min cooling rate.
estimation from Figures 6.2(a) and (b). The thickness of the PTFE sample was chosen to accommodate the size of the temperature probe.

Table 6.2. True sample temperature $T_{\text{sample}}$ with regard to the imposed $T_{\text{chamber}}$ after steady-state conditions had been reached. The accuracy for $T_{\text{chamber}}$ setting is $\pm 0.1 ^\circ C$.

<table>
<thead>
<tr>
<th>$T_{\text{chamber}}$ ($^\circ C$)</th>
<th>$T_{\text{sample}}$ ($^\circ C$)</th>
<th>Accuracy (K)</th>
<th>$\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>165</td>
<td>$\pm 1$</td>
<td>15</td>
</tr>
<tr>
<td>120</td>
<td>112</td>
<td>$\pm 0.6$</td>
<td>8</td>
</tr>
<tr>
<td>114</td>
<td>107.5</td>
<td>$\pm 0.5$</td>
<td>6.5</td>
</tr>
<tr>
<td>110</td>
<td>103.5</td>
<td>$\pm 0.5$</td>
<td>6.5</td>
</tr>
<tr>
<td>109</td>
<td>102.5</td>
<td>$\pm 0.5$</td>
<td>6.5</td>
</tr>
<tr>
<td>107</td>
<td>101</td>
<td>$\pm 0.5$</td>
<td>6</td>
</tr>
<tr>
<td>103</td>
<td>97</td>
<td>$\pm 0.5$</td>
<td>6</td>
</tr>
<tr>
<td>99</td>
<td>93</td>
<td>$\pm 0.5$</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>29</td>
<td>$\pm 0.2$</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6.2 demonstrates that the discrepancy between $T_{\text{chamber}}$ and $T_{\text{sample}}$ in steady-state condition becomes larger for higher temperatures. This is expected from the increasing heat loss at elevated temperatures. The true sample temperature calibration is very important for the EIC experiments, because the crystallization kinetics of PB-1 is extremely sensitive to the degree of undercooling. Yet, the determination of $T_{\text{sample}}$ from the external temperature probe certainly involves some errors. From repeated runs, this error is determined to be $\pm 0.5 ^\circ C$ at temperatures used for the EIC experiments. In the following text, the stated temperature always refers to the sample temperature $T_{\text{sample}}$ unless otherwise stated.

6.1.3. Annealing Conditions

For the stretching experiments, the sample was always annealed at $T = 165 ^\circ C$ ($T_{\text{chamber}} = 180 ^\circ C$) for 10 minutes to erase the effect of pre-flow and thermal history. In Figure 6.3, these annealing conditions were compared with two others and no significant difference was observed in the resulting viscosity curves (within 10% experimental error).
Another potential problem during annealing is the sagging of the sample. By testing different annealing times at 165 °C (Figure 6.4), it was found that BR200 has a sufficiently high sagging resistance due to its high zero shear viscosity, and the small change in sample shape during the annealing phase (visible when the oven is opened after the experiment) did not influence the results. An elongational viscosity curve obtained using the Meissner-type rheometer (RME) is also included in the figure, and it is evident that there is a good agreement for the two methods.

In Figure 6.4, the curves show a slight strain-hardening near the end of the run, which is normally not expected for linear samples. However, BR200 has a very high molecular weight, which may also induce similar effects (through entanglements) as branching does. When the chains become stiffer at undercooled condition, this strain-hardening will be more pronounced, as seen later in Figure 6.9.
After annealing at 165 °C, the sample was cooled to the crystallization temperature with a cooling rate of −15 K/min. As seen from Figure 6.2, the response of $T_{\text{sample}}$ is slower than that of $T_{\text{chamber}}$, and a significant time is required for the sample to reach a stable temperature. Therefore, to conduct an isothermal experiment, a delay time has to be imposed after $T_{\text{chamber}}$ has reached the specified temperature. In the next section below, it will be explained why the selection of delay time is not trivial, and why in Figure 6.2, the stretching is started before the sample really reaches a stable plateau. However, it is important to note that Figure 6.2 the graph provides a conservative estimate of this delay time, because the BR200 sample is half as thick as the PTFE sample (with similar heat conductivities). Therefore, the response time for the BR200 slab is one quarter that of PTFE, and this means $T_{\text{sample}}$ will be closer to the plateau in the experiments using BR200.

6.1.4. Effect of Delay Time on Transient Elongational Viscosity

The delay time is also important to reach an even temperature distribution across the sample, since the parts of the sample in contact with the cylinders (see Figure 6.1) have a slower cooling rate. Because of their mass, the cylinders retains heat during the cooling
stage and hence the side parts of the sample also cool slower compared to the suspended middle part. Several tests by placing the external temperature probe position at the side instead of the centre of the sample prove this point. However, if the chosen delay time is too long the sample may show quiescent crystallization in its undercooled state before the actual measurement at an imposed strain rate is started. Therefore, a delicate compromise is necessary between having a fully stable sample temperature and avoiding quiescent crystallization prior to stretching.

![Graph showing transient elongational viscosity at 93 °C with various delay times](image)

**Figure 6.5.** Transient elongational viscosity at 93 °C with various delay times $t_d$ before stretching at $\dot{\varepsilon} = 0.3 \, s^{-1}$.

Figure 6.5 shows how the delay time affects the $\eta_E(t)$ curves. The moment at which the stretch is started $(t_0)$ corresponds to the time when $T_{chamber}$ has reached the crystallization temperature plus the delay time $t_d$ (refer to Figure 6.2). The occurrence of necking for $t_d = 0$ visibly affects the shape of the viscosity curve. First, an apparent decrease in elongational viscosity is observed. However, the stress in the necking region becomes very large as the sample is stretched with the same strain rate; this induces crystallization and consequently a viscosity upshoot, which may happen later had the necking not occurred. The transition between necking and crystallization is signified by a sharp minimum in the viscosity curve. Necking always starts close to one of the drums, which supports the idea that it stems from temperature inhomogenities in the sample. For $t_d = 5$
minutes, the curve shows a smooth viscosity upshoot without signs of necking. However, for \( t_d \) larger than 10 minutes, an initial viscosity much larger than the expected value is observed, which indicates that crystallization has already started.

It is evident that the selection of the delay time is not trivial. Since there is no distinct change in slope before \( T_{sample} \) reaches a plateau, the delay time cannot simply be determined from Figure 6.2(b). However, a delay time \( t_d = 5 \) minutes appears as a reasonable compromise to define the proximity of a steady crystallization temperature, and this was chosen for crystallization experiments at other temperatures.

### 6.2. Results

#### 6.2.1. Determination of Onset Time and Checking of Reproducibility

The method to determine an elongation flow-induced crystallization onset time \( t_{on,el} \) is described in Figure 6.6. The broken line represents the transient elongational viscosity \( \eta(t) \) for the limit of small strain rates. First, the \( \eta(t) \) curve was calculated based on the discrete relaxation spectrum at 150 °C, where the polymer is in a melt state. The spectrum was calculated from the storage and loss moduli data (\( G' \) and \( G'' \), respectively).

\[
\eta(t) = \sum_{i=1}^{n} H_i \cdot \tau_i \cdot \left(1 - e^{-t/\tau_i}\right),
\]

- \( H_i \) = relaxation modulus of the \( i \)-th mode
- \( \tau_i \) = relaxation time of mode \( i \)-th mode
- \( i \) = number of modes (in the calculation \( i = 10 \))

Then, the spectrum was shifted to the experimental temperature (e.g. 93 °C in Table 6.3) using the Arrhenius shift factor \( a_T \) as shown in Table 6.1. The onset time is determined by drawing a line \( 6 \eta(t) \) (i.e. \( 2 \times 3 \eta(t) \)) and locating the intersection between this line and the upshoot observed in the experimental transient elongational viscosity. The factor two was arbitrarily chosen, based on the observation that at this stage the elongational viscosity has reached a significant upshoot, but not yet too far from its initial undercooled melt state. Since the upshoot in \( \eta_E \) is sharp, there will be no significant shift in onset
time had a higher factor been selected. The same factor was also used to determine the crystallization onset time in previous SIC experiments. Although it has not been confirmed that at this point the degree of crystallinity in the sample is the same in shear and elongation, choosing the same factor facilitates an easier comparison between EIC and SIC results. The comparison of three runs A, B, and C in Figure 6.6 indicates an excellent reproducibility of the experiment.

Table 6.3. Relaxation spectrum of BR200 at 93 °C, with $i$ as the number of modes.

<table>
<thead>
<tr>
<th>Relaxation time $\tau$ (s)</th>
<th>Relaxation strength $g_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.59 \times 10^{-2}$</td>
<td>$6.02 \times 10^4$</td>
</tr>
<tr>
<td>$1.35 \times 10^{-1}$</td>
<td>$2.85 \times 10^4$</td>
</tr>
<tr>
<td>$7.81 \times 10^{-1}$</td>
<td>$3.15 \times 10^4$</td>
</tr>
<tr>
<td>$5.14 \times 10^{0}$</td>
<td>$2.04 \times 10^4$</td>
</tr>
<tr>
<td>$1.19 \times 10^{1}$</td>
<td>$5.70 \times 10^3$</td>
</tr>
<tr>
<td>$3.20 \times 10^{1}$</td>
<td>$1.00 \times 10^4$</td>
</tr>
<tr>
<td>$1.04 \times 10^{2}$</td>
<td>$5.88 \times 10^4$</td>
</tr>
<tr>
<td>$1.92 \times 10^{2}$</td>
<td>$3.06 \times 10^3$</td>
</tr>
</tbody>
</table>

Figure 6.6. Determination of $t_{on,el}$ and data reproducibility for BR200 stretched at 93 °C and 0.3 s$^{-1}$ ($t_d = 5$ minutes).
6.2.2. **Quasi-quiescent Crystallization**

Quasi-quiescent crystallization means that the sample crystallizes as if it were in a quiescent state, although flow is present. Hence, the flow rate has to be low enough to allow the polymer chains to remain in a relaxed state. Since the imposed flow does not affect the crystallization kinetics, there should be no difference whether the flow is shear or elongational. This yields an important check for the soundness of the quasi-quiescent crystallization experiments.

The actual sample temperature protocol again becomes a crucial factor, because there has to be a match between $T_{\text{sample}}$ in shear (plate-plate) and EVF geometry. For the plate-plate geometry, there is first the option to control the fixture temperature $T_{\text{tool}}$, which corresponds to the temperature of the lower plate and closely represents $T_{\text{sample}}$ situated directly above it (within $\pm 0.1 \, ^\circ\text{C}$ at steady-state), and second to control $T_{\text{chamber}}$ (like when using EVF). The $T_{\text{sample}}$ cooling profile as shown in Figure 6.2(b) for EVF can be mimicked for the shearing experiments using $T_{\text{tool}}$ as the controller, by applying different cooling slopes. This temperature protocol is described in Table 6.4 for experiments at 97 °C and 101 °C:

<table>
<thead>
<tr>
<th>Step</th>
<th>Experiment at $T = 97 , ^\circ\text{C}$</th>
<th>Experiment at $T = 101 , ^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Annealing at 165 °C, 10 min</td>
<td>Annealing at 165 °C, 10 min</td>
</tr>
<tr>
<td>(2)</td>
<td>Cool to 117 °C, 8.1 °C/min</td>
<td>Cool to 121 °C, 9.2 °C/min</td>
</tr>
<tr>
<td>(3)</td>
<td>Cool to 102 °C, 3.3 °C/min</td>
<td>Cool to 103 °C, 3.0 °C/min</td>
</tr>
<tr>
<td>(4)</td>
<td>Cool to 101 °C, 2.0 °C/min</td>
<td>Cool to 102 °C, 2.0 °C/min</td>
</tr>
<tr>
<td>(5)</td>
<td>Cool to 97 °C, start shearing</td>
<td>Cool to 101 °C, start shearing</td>
</tr>
</tbody>
</table>

In Figure 6.7, the resulting $T_{\text{sample}}$ profiles for three different cases are shown, with the aim of cooling $T_{\text{sample}}$ from 165 °C to 101 °C but by switching from EVF to plate-plate and from using $T_{\text{chamber}}$ to $T_{\text{tool}}$ as the controller. When $T_{\text{chamber}}$ is set as controller, a cooling rate of $-15 \, \text{K/min}$ is used, like in Figure 6.2(b). However, when $T_{\text{tool}}$ is set as
controller, the special temperature protocol described in Table 6.4 is applied. Figure 6.7 first demonstrates that the $T_{\text{sample}}$ profiles during cooling in EVF and plate-plate geometries can be matched (using $T_{\text{chamber}}$ as controller in both cases). In addition, it is also shown that the special temperature protocol works reasonably well, although the curve is not as smooth due to approximation by using three different cooling slopes. The time zero for the start of shearing or stretching is set as $t_0 = 660$ s, which already includes the delay time $t_d = 5$ min when $T_{\text{chamber}}$ is used as the controller.

![Sample temperature profiles in EVF and plate-plate geometries during cooling from $T_{\text{sample}} = 165$ °C to $T_{\text{sample}} = 101$ °C, using different temperature control modes.](image)

Figure 6.7. Sample temperature profiles in EVF and plate-plate geometries during cooling from $T_{\text{sample}} = 165$ °C to $T_{\text{sample}} = 101$ °C, using different temperature control modes.

Figure 6.8 displays the transient viscosities $\eta_E(t, \varepsilon)$ and $\eta(t, \gamma)$, respectively, corresponding to the three cases in Figure 6.7 and sheared/stretched at $10^{-3}$ s$^{-1}$. This deformation rate was chosen because it has been shown in Chapter 5.1 that for shear, $10^{-3}$ s$^{-1}$ is low enough to be in the quasi-quiescent region. The important evidence from this graph is the excellent agreement between the three curves with regard to the time when the shear/elongational viscosity shows an upshoot.

The reproducibility is very good provided that the sample temperature is the same for every run. This condition is easier to fulfil when $T_{\text{tool}}$ is used as the controller. In this case, the error bar is estimated to be 10%. However, when $T_{\text{chamber}}$ is used as the controller, there is a greater possibility for $T_{\text{sample}}$ to vary (see Table 6.2) and in quasi-
quiescent state, where the driving force for crystallization comes solely from the degree of undercooling, a substantial shift in the onset time is expected even for a temperature difference of 0.5 °C. Previous results from SIC experiments predict an exponential trend for the quasi-quiescent onset time data with increasing temperature. From this trend, the variation that comes with 0.5 °C difference is around 16% for $T = 99 – 107 °C$. Based on these estimates, an error bar of 15% is reasonable when comparing results from different methods like in Figure 6.8.

![Figure 6.8. Viscosity curves obtained from shearing/stretching experiments at shear/strain rate = 0.001 s$^{-1}$ and $T_{sample} = 101 °C$, following different temperature control modes but comparable temperature profiles as given in Figure 6.7.](image)

It is important to note that the cooling history of the sample here is different to that described in Chapter 4.1, in which $T_{tool}$ was used as controller and only one cooling slope of $-15$ K/min was applied. However, provided that the temperature at the start of shearing is the same, the two cooling histories do not have a significant effect on the onset time (within 5% error).

6.2.3. Elongation-Induced Crystallization

For these experiments, the temperature protocol shown in Figure 6.2(b) is applied, using $T_{chamber}$ as the controller. Transient elongational viscosities $\eta_E$ at strain rates ranging from $10^{-5} – 10$ s$^{-1}$ for $T = 101 °C$ and 97 °C are given in Figures 6.9(a) and (b),
respectively. At low strain rates (0.0001 – 0.1 s\(^{-1}\)), the initial part of the elongational viscosity curve corresponds well to the level predicted at that temperature (estimated by shifting the \(3\eta(t)\) data at 150 °C). After a certain time, an upshoot is observed, and the onset time \(t_{on,el}\) can be determined as illustrated in Figure 6.6. However, for strain rates of 0.01 s\(^{-1}\) and 0.03 s\(^{-1}\) at 101 °C, no \(t_{on,el}\) can be determined because the maximum Hencky strain achievable in EVF had been reached before the sample exhibited an upshoot.

At high strain rates attempted (0.3 s\(^{-1}\) and higher), the curves already show a strong upward deviation from the predicted level of elongational viscosity even at early stage (before the sharp upshoot). While the sharp upshoot is attributed to the crystallization of sample, the earlier deviation is expected to come from strain-hardening effect. The method to determine the onset time from the \(6\eta(t)\) line, as explained before, is in this case not appropriate because it does not take into account the elongational viscosity increase from strain-hardening. Therefore, the shape of the curve for a strain-hardening sample at a particular temperature and strain rate has to be predicted first. This is done using the MSF (Molecular Stress Function) model developed by Wagner et al. (2001).

The recent version of the MSF model incorporates the convective constraint release (CCR) and introduces improvement in capturing the rate of strain hardening in uniaxial, biaxial, and planar elongations of polydisperse samples. Olley (2005) gives a short review on the MSF models and compare them with KBKZ model. The extra-stress term \(\tau(t)\) constitutes the MSF model and is given as follows:

\[
\tau(t) = \int_{-\infty}^{t} m(t-t')S_{MSF}(t')dt',
\]

\[
S_{MSF} = 5f^2\left(\frac{\mathbf{u}'\mathbf{u}'}{\mathbf{u}'^2}\right),
\]

\(S_{MSF}\) = strain measure, related to the Doi-Edwards strain function \((S_{DE})\) through \(S_{MSF} = f^2S_{DE}\).

\(m(t-t')\) = memory function between time \(t'\) in the past and current time \(t\).

\(\mathbf{u}'\) = deformed vector.
\( f \) = the molecular stress function, which is the inverse of relative tube diameter.
\( f^2 \) = square of the molecular stress function, corresponding to the affine deformation of the average tube cross section.

The only adjustable parameter in the model is \( f_{\text{max}}^2 \), which sets the attainable maximum value of \( f^2 \). This parameter is characteristic of a polymer melt.

Figure 6.9. Transient elongational viscosity curves for BR200 stretched with various strain rates, at (a) 101 °C and (b) 97 °C.
In Figure 6.10(a), the experimental elongational viscosity curves at 101 °C and strain rates from 0.3 s⁻¹ to 10 s⁻¹ are compared with those predicted from MSF simulations. For the simulations, the relaxation time spectrum of BR200 at the relevant temperature (e.g. 101 °C) must be provided. As has been explained earlier (refer to Table 6.3), the relaxation spectrum at 150 °C is first obtained from experimental data, then shifted to 101 °C using an Arrhenius shift factor $a_T$. Several values of $f_{\text{max}}^2$ ranging from 9 to 30 were tested to fit the elongational viscosity curve at 10 s⁻¹. The value of $f_{\text{max}}^2 = 18$ gives the best fit, and as can be seen from Figure 6.10(a), it also predicts the strain-hardening behavior very well for the other strain rates.

As the sample solidifies, there is a clear deviation from the MSF-predicted curve. Similar to the normal procedure, here the onset time is determined by multiplying the MSF-predicted curve by two and finding the intersection with the experimental curve, as described in Figure 6.10(b) for the strain rate of 10 s⁻¹. The same procedure is performed for the data at 97 °C and strain rates of 1 s⁻¹ to 10 s⁻¹.

Above a certain strain rate, the elongation flow starts to enhance the crystallization kinetics and causes the EIC onset time $t_{\text{on,el}}$ to decrease. A systematic reduction in $t_{\text{on,el}}$ is observed up to the maximum strain rate tested (10 s⁻¹), where the time scale of the experiment is below 1 s. Figure 6.11 shows the EIC onset times $t_{\text{on,el}}$ at 97 °C and 101 °C, decreasing exponentially in the flow-induced crystallization region. At high strain rates, the influence of temperature is overcome by the kinetic driving force, and there is not much difference between the onset times at the two temperatures.
Figure 6.10. (a) Comparison of MSF simulation results and experimental data for BR200 at 101 °C, and (b) determination of crystallization onset time.
and 97 °C are mentioned earlier, in SIC on time.

In Figures 6.12(a) and (b), the EIC onset time data ($t_{on,el}$) at 101 °C and 97 °C are compared with SIC data at the same temperatures ($t_{on,sh}$). As mentioned earlier, in SIC also a factor of 2 in viscosity upshoot is used to determine the crystallization onset time. Theoretically, when comparing a shear rate- and strain rate-dependent property (in this case the onset time) on one graph, the strain rate has to be multiplied by $\sqrt{3}$ because it is “stronger” than the shear rate. However, this factor is relatively small and in the following figures the onset time data are compared at the same nominal values of shear and strain rates.

Figures 6.12(a) and (b) clearly demonstrate that in flow-induced crystallization regime, elongation is more effective than shear in enhancing the crystallization kinetics. The difference between the onset times in shear and elongation increases for larger rates, and at 0.3 s$^{-1}$ the gap is almost one decade. The maximum shear rate that can be achieved in ARES using the plate-plate geometry is limited because the sample is thrown out of the plates if the shear rate is too high. Therefore, in Figure 6.12(a) several data points obtained using a concentric cylinder (Couette-type) rheometer are added to those obtained with standard plate-plate geometry. Actually for both methods, shearing at high
rates would create secondary flows. With the concentric cylinder rheometer, shearing above 50 s\(^{-1}\) results in significant shear heating. However, within the range of shear rates considered here, the climb in viscosity signal is well-defined to enable the determination of the onset time. In **Chapter 5.2.3** it has been shown that the onset times from both shearing devices overlap at the same shear rate and temperature.

![Graph](image)

**Figure 6.12.** (a) EIC and SIC onset time data for BR200 at 101 °C. Crosses are data points obtained by concentric cylinder (Couette) rheometer (see Chapter 5.2.2).

(b) EIC and SIC onset time data for BR200 at 97 °C.
Figures 6.13(a) and (b) show the amount of total strain when the onset time is achieved, for different strain and shear rates, respectively. Apparently, in the case of EIC the total strain at the onset time reaches a constant value of 4 outside the quasi-quiescent regime. On the other hand, in SIC the total strain continues to increase with increasing shear rate, although the slope is less compared to that in the quasi-quiescent state.
6.3. Discussion

The determination of crystallization onset time from the upshoot in transient elongational viscosity is valid only if the upshoot can be attributed to crystallization and not to strain-hardening caused by entanglements. Although BR200 does not contain branched molecules, it contains long molecules that may lead to significant number of entanglements. At low temperatures the entanglement effect becomes pronounced, as seen in Figures 6.9(a) and (b) for strain rates above 0.3 s\(^{-1}\). The strain-hardening due to entanglements effect can be predicted using the MSF model for polydisperse melts (Wagner, 2001). In this case, the simulation was done for a linear polymer, which corresponds to the sample at hand. The model is able to predict the strain-hardening behavior of BR200 very well. As crystallization starts, the curve deviates from the MSF prediction and exhibits a much sharper increase in elongational viscosity. Hingmann and Marcinke (1994), for example, have observed that in the case of strain-hardening, the total Hencky strain at the point of deviation from linearity is approximately 1, independent of the strain rate. In Figures 6.9(a) and (b), this strain-hardening deviation at \(\varepsilon = 1\) is observed for strain rates of above 0.3 s\(^{-1}\). At lower strain rates, the curves conform to the linear elongational viscosity curve until crystallization takes over – where the Hencky strain reaches a constant value of 4.

As seen in Figure 6.11, beyond a certain strain rate the elongational flow results in an exponential decrease of the crystallization onset time. This is caused by the coil-stretch transition of the polymer chains, which brings them closer to the final, oriented state required in crystallization (Gedde, 1995). In the limit of very small strain rates, the flow does not contribute enough kinetic driving force and the polymer chains have enough time to relax back to their coiled state, resulting in a quasi-quiescent crystallization. As shown in Figure 6.8, in such case the type of flow (shear or elongational) does not affect the crystallization onset time. This fact is important as a basis to compare crystallization onset times at higher shear/strain rates.

In the flow-induced crystallization regime, it is well known that elongation is a more effective flow to induce crystallization compared to shear. In Figure 6.12, the EIC and
SIC onset times differ as much as one decade for even a relatively low rate of 0.3 s\(^{-1}\). It is also observed that the critical rate required to trigger flow-induced crystallization in shear (0.01 s\(^{-1}\)) is approximately one magnitude higher than that in the case of elongation (0.001 s\(^{-1}\)).

The different trends seen for EIC and SIC regarding the total strain at the onset time is interesting. It is well-known that for a significant flow magnitude, increasing shear rate results in shear thinning of the sample, while elongation induces strain-hardening. The paper of Zülle et al. (1987) discusses the different sample behavior under simple elongation and simple shear, relating it to the deformation histories. It was found that for viscoelastic materials the first principal stretch rate \( \dot{\lambda}_i(t) \) is very different for the two flow types. In this respect the simple shear is analogous to a planar extension with the extension rate decreasing continuously with time. Considering this fact, it is reasonable to find the increasing total strain (at \( t_{onset} \)) with shear rate. On the other hand, the experimental data from Lagasse and Maxwell (1976) suggest that in SIC the total strain also approaches a constant value at high shear rates, although the onset time is not clearly defined in their experiment.

Several studies support the experimental observations given in this paper. Termonia (2000) studied the coil-stretch transition induced by shear flows or elongational flows in dilute polymer solutions. Using a version of the Monte-Carlo lattice model, it is predicted that the coil-stretch transition is sharper and occurs at a much lower flow rate in the case of elongational flow. By observing the distribution of radius of gyration of the chains, it is shown that elongation flow results in more chains with an extended conformation, whereas in shear flow the portions of coiled and extended chains are more equally distributed.

Recently, Coppola et al. (2001) proposed the use of microrheological modelling to predict crystallization onset times in EIC and SIC. The model was based on the free-energy function of Doi-Edwards theory, developed by Marrucci and Grizzuti (1983). According to the model, flow contributes to the increase in free energy (\( \Delta G_f \)) – in
addition from the increase in free energy due to undercooling ($\Delta G_q$) – thereby inducing faster crystallization. Also in this case, elongational flow has a greater effect than shear flow. In the graph of onset time vs. shear/strain rate two plateaus are predicted, one in quasi-quiescent regime and another one at very large rates. The argument for the second onset time plateau is that the chains are stretched to the maximum and further increase in shear/strain rate will not enhance the crystallization kinetics further. However, experimentally this regime is difficult to reach because of the low time scale and high deformation rates involved. This is also where the model may become unrealistic, because various side-effects (e.g. secondary flows, shear heating) have to be taken into account that contribute to the clearly observable, “macroscopic” crystallization event in the sample. In the current paper no sign of this second plateau is evident, and a decrease in onset time is observed up to the highest strain rate attempted, which is 10 s$^{-1}$.

Previously in Chapter 5.1.2, it was proposed that through a normalization method with respect to quasi-quiescent onset time, a temperature-invariant curve of onset time vs. shear rate can be constructed and the data points fitted with a Cross function. Here, the method is applied to create a temperature-invariant representation of the onset times in EIC, as shown in Figure 6.14. In this case, the normalization method reduces the convergence of data points in flow-induced region, because in Figure 6.11 (the non-normalized graph) these points already collapse due to much larger influence of elongational flow compared to degree of undercooling. However, the quality of the Cross fit is comparable to that in the case of SIC. In Figure 6.14, the deviation of the data points does not seem to depend on the strain rate, up to the largest strain rate attempted (10 s$^{-1}$). The SIC T-invariant curve is also included in the graph. Both curves show a slope of approximately -1.

In a paper by Samon et al. (2002), a slope of -0.974 is shown for the plot of crystallization onset time against take-up speed in melt spinning experiment, for four chemically different polymers (HDPE, PVDF, PA6, POM) having similar melt viscosities. The take-up velocities ranged from 10 to 1000 m/min, which fall in the low to moderate range for melt spinning process but translate to higher strain rates than those
attempted here. Although the temperature profiles of the sample are very different in melt spinning and EVF experiments (in melt spinning the temperature varies with distance from the spinneret), the similar trend of slope \( \approx 1 \) indicates that the T-invariant curve can be extended into even higher strain rates.

![T-invariant Curve](image)

**Figure 6.14.** Temperature-invariant representation of EIC onset time data obtained at 97 °C and 101 °C and strain rates \( 10^{-4} \) – \( 10^2 \) s\(^{-1} \), compared with SIC temperature-invariant curve.

From the comparison it is again clear that elongation flow has a much stronger effect on crystallization than shear flow. To achieve a 100-time reduction in onset time (compared to the quasi-quiescent state), for example, the shear flow has to be around one degree of magnitude higher than elongation flow. It is important to note that these curves have been tested in a limited range of temperature (99 °C – 107 °C for SIC and 97 °C – 101 °C for EIC). However, in this range one can already see a large variation in quasi-quiescent onset times. As the purpose of constructing a temperature-invariant curve is actually to characterize the flow-induced crystallization behavior of a sample, the curves have to be compared with those for other samples. Unfortunately, in the case of EIC, the choice of sample is more restricted due to requirement of high viscosity to prevent sagging.

### 6.4. Conclusions

As shown in the Experimental and Results sections, several important challenges in performing the EIC experiment with EVF are associated with the temperature of the
sample. First, the sample must be able to withstand the annealing stage without sagging too much that it affects the subsequent measurement. In addition, careful temperature calibration is necessary to know the true sample temperature, and application of a delay time before stretching is required for an isothermal experiment. Because of this necessary delay time, however, the range of experimental temperature is limited to temperatures rather close to $T_{m2}$, otherwise crystallization already sets in during the delay time.

An important part of this paper is the comparison of onset time data in EIC and SIC. It has been shown that in quasi-quiescent condition the crystallization onset times in shear and elongation coincide. In the flow-induced crystallization regime, elongational flow is more effective in enhancing crystallization kinetics compared to shear flow, as seen from the more significant reduction in onset time. This trend increases in magnitude as the deformation rate increases. The normalization method applied previously for SIC also works for EIC in constructing a temperature-invariant curve. The curve for SIC exhibits larger plateau region than that for EIC, indicating that crystallization is more sensitive to elongational flow. Theoretically, a second plateau is expected at very high shear/strain rates, where the polymer chains are stretched to a maximum extent and no further reduction in onset time is possible. However, in the range of deformation rates attempted in this paper, such a plateau is not observed.

As a further step, samples having other molecular weights (but they have to be sufficiently high) or characteristics should be tested using the EVF. In addition, the EIC onset time data can be compared with the prediction from microrheological model (Coppola et al., 2001), which has been shown to work well in predicting SIC behavior of several polymers.


7.0 MODELING OF FLOW-INDUCED CRYSTALLIZATION

7.1 Introduction

In the current study, the main concern is to develop experimental methods, by which crystallization under strong flow rates can be investigated. While experimental techniques and results are important, an insight into the other side of crystallization study – modeling – is also necessary. In this case, the aim is to construct a robust model, by which the crystallization onset time and distribution of crystal morphology can be predicted. Ideally, the model should contain as few adjustable parameters as possible, and use the parameters representing the sample properties, which can be derived from standard measurements.

Models that predict the behavior of the polymer melt under flow (shear and elongational) are already well-established. Two basic theories of polymer mechanics are widely known and become the guiding principles for the subsequently introduced models:

- Reptation theory of de Gennes (1971) and Doi and Edwards (1986), more popularly known as the “tube model”. The polymer chain is envisioned as moving by reptation motion inside a tube of certain diameter, and its freedom is restricted by the presence of other tubes.

- Network theory, introduced by Lodge (1964). Here, the sample is constructed of a changing network, and its rheology depends on the balance between the creation and destruction of network links.

These theories gave rise to some quite recently proposed models, such as the “Pom-Pom” model (McLeish and Larson, 1998) based on the reptation theory and the Phan-Thien – Tanner (PTT) model (Phan-Thien and Tanner, 1977) based on the network theory.

There are many variations and improvements to these models introduced in the subsequent years. For example, one popular variant of the Pom-Pom model is the “Extended Pom-Pom” or XPP model (Verbeeten et al., 2001). As no model is yet proven to work in all situations, there is an ongoing debate on which model works best. A recent article by Tanner (2006) compares the PTT and XPP models and suggests that the models support each other and can be reconciled. In any case, the understanding of how polymer
chains behave in melt condition under flow still presents a challenge. For crystallizing samples, however, the complexity of the problem is compounded by the interplay between solidification process and changes in rheological properties.

The crystallization kinetic aspect of FIC models is generally based on the equations already developed for crystallization under quiescent conditions, such as the KAE (Kolmogoroff-Avrami-Evans) approach (briefly covered in Chapter 2: Literature Review), Schneider differential equations (Schneider et al., 1988), and Nakamura isokinetic model (Nakamura et al., 1972). Initially, Flory (1947) already attempted to modify the quiescent crystallization kinetics to account for chain stretching under flow by introducing the melting point elevation theory. However, his proposition does not address the coupling between rheology and evolution of crystallization kinetics. Subsequent experiments also showed that only high-speed fiber spinning would create a stress level high enough for a measurable melting point elevation. Therefore, there is a need for FIC model improvement and it is mainly since the 1990s that a series of FIC models incorporating rheology began to develop.

### 7.2 Flow-Induced Crystallization Models

Prior to the profusion of FIC models, strain-induced crystallization models meant for cross-linked rubber networks already exist. In this case, stretching increases the distance between the cross-links, reducing the entropy of the polymer chain between the cross-links (Gaylord and Lohse, 1976). The main difference between rubber networks and polymer melts is the presence of the physical cross-links in rubber and the geometrical entanglements in melts. Consequently, the model must be altered to account for this.

It is believed that the main effect of flow is to increase the nucleation rate (Lagasse and Maxwell, 1976), although some researchers claimed that the growth rate is also increased to a lesser degree (Duplay et al., 2000). Therefore, one of the main challenges in constructing the model is to pinpoint the dependence of the flow-induced nucleation rate ($\dot{N}_f$) on flow variables. Tanner and Qi (2005) list seven parameters on which the
equations for $\dot{N}_f$ have been developed by various researchers, and there is at least one more that can be added to the list:

1. Shear rate (Eder and Janeschitz-Kriegl, 1997).
3. Stress (Doufas et al., 2000).

These models are mainly based on shear-induced crystallization experiments, with the exceptions of (3), (4), and (5), which are oriented towards melt-spinning applications.

In the following sections, some of these models are briefly described, highlighting their advantages, limitations, and compatibility with experimental results.

8.2.1 Shear-rate dependence

Based on the short-term shearing experiments developed by the research group at Linz (Liedauer et al., 1993), Eder and Janeschitz-Kriegl (1997) derived a relationship that links the shear rate to the formation of highly-oriented and finely-grained layers in sheared samples (see Figure 2.10). A critical parameter of $\dot{\gamma}^4 t_s$ (where $t_s$ is shearing time) was found to be responsible for the boundary layer between highly-oriented and finely-grained layers, while for the border between finely-grained layer and the spherulitic core, the parameter is $\dot{\gamma}^2 t_s$. The latter form corresponds to the proposed normalization parameter for the x-axis in the current work ($\dot{\gamma} t_{on,q}^{0.5}$), as explained in Section 5.1.4.

In the model, the nucleation rate is equal to the sum of quiescent nucleation rate $\dot{N}_o$ and shear-induced nucleation rate $\dot{N}_f$. For the quiescent nucleation rate $\dot{N}_o$, the classic
Kolmogoroff-Avrami-Evans (KAE) and its derivative variant, Schenider’s rate equations, were used, while the nucleation rate due to flow $\dot{N}_f$ follows the differential equation:

$$\dot{N}_f = \left( \dot{\gamma} / \dot{\gamma}_n \right)^2 g_n - N_f / \lambda_f,$$

where $\lambda_f$ stands for a relaxation time (which can be assumed to be infinite for the case of steady shear), $N_f$ the number of nuclei per unit volume, $\dot{\gamma}_n$ a characteristic shear rate, and $g_n$ a pre-factor with dimensions $m^{-3}s^{-1}$.

While Equation 7.1 establishes a clear and simple relationship between shear rate and nucleation rate, it has a phenomenological origin and the physical explanation offered is not fully satisfactory. Therefore, its use as a predictive tool is limited. Moreover, the dependence on temperature is not included in the equation, although it is shown that this dependence is small for the experimental conditions tested in Eder and Janeschitz-Kriegl (1997). For other polymers, problems might also occur with the determination of $\dot{\gamma}_n$ from experiments, if the boundaries between layers cannot be clearly defined. This problem was encountered by the same research group (Braun et al., 2003) when using PB-1 as the sample.

8.2.2 Continuum model

The continuum model introduced by Doufas et al. (2000) is a macroscopic model, combining irreversible thermodynamics through the continuum Hamiltonian/Poisson bracket formalism with the Avrami kinetic equation for polymer crystallization. A continuum model means that the details of molecular mechanisms of FIC or the crystal morphology are not taken into consideration. Instead, it looks into the “macroscopic” characteristics of overall crystallization kinetics and the rheological/rheooptical behavior of semicrystalline systems.

An earlier work by Bushman and McHugh (1996) already dealt with the development of a continuum model, however there is only one constitutive equation for the amorphous phase. In Doufas’ continuum model, both the amorphous and crystalline phases are
accounted for. A modified Giesekus fluid (Giesekus, 1982) is assumed for the amorphous phase, while the crystalline phase is modeled as a collection of multibead rigid rods that grow and orient in the flow field.

From the constitutive equations and by constructing the Hamiltonian of the semicrystalline system, evolution equations for three dimensionless structural variables are obtained. These variables are \( c^* \) (conformation tensor), \( S \) (orientational tensor), and \( \phi \) (crystallinity). The model is deemed to be self-consistent, because in the absence of flow, the equation reduces to the modified Giesekus model for the melt, and quiescent crystallization follows the standard Avrami kinetic equation.

Fitting with experimental data involves two adjustable parameters, namely \( \lambda_{cr,max} \) (the crystalline relaxation time) and \( \zeta \) (the coupling exponent). As can be seen in Figures 7.1(a) and (b), the selection of \( \zeta \) has a significant influence on the curves of crystallinity vs. dimensionless time and of induction time vs. shear rate, although for the latter the qualitative trend is preserved. It also decides the shape of the stress-crystallization time curve. On the other hand, \( \lambda_{cr,max} \) value only influences the stress-crystallization time curve and not the two other curves.
Figure 7.1 Effect of the coupling parameter $z$ on (a) crystallization kinetics, and (b) reduction of induction time with shear rate (Doufas et al., 2000).

The main advantages of the continuum model are its proven self-consistency in coupling crystallization kinetics and rheological behavior, and the relatively small computation time. However, while the model has been shown to successfully predict the experimental data of Bushman and McHugh (1997) in planar extensional flow, for the case of shearing this is yet to be tested. In fact, an evaluation by Tanner (2005) seems to point that the agreement with SIC induction times is not that good, probably because of the different assumption in calculating the total stress level (see Section 7.2.3 below).

8.2.3 FIC model based on suspension theory

The suspension theory employed by Tanner (2002, 2003) describes a system of rigid spheres (crystallites) embedded in a fluid matrix. For the simplest case, the fluid can be considered Newtonian (Tanner, 2002). In his follow-up paper on the same topic (Tanner, 2003), the matrix behavior is assumed as linear viscoelastic, which is true for small-strain
An option for non-linear generalization is also discussed by describing the amorphous phase as a PTT or General Network model.

For modeling purposes, the main problem lies in computing the total stress as crystallization progresses, i.e. as rigid spheres are introduced into the amorphous matrix. If a simple addition rule is assumed, the total stress will take the form:

$$\tau = \tau_a + \tau_c,$$  \hspace{1cm} (7.2)

where \( \tau_a \) and \( \tau_c \) are stress contributions from the amorphous and crystalline phases, respectively. The approach adopted by Doufas et al. (2000) uses this assumption. However, this “continuum model” implies a mixture on the molecular scale of the crystalline and amorphous components at each point, whereas microscopic observations show that a more realistic description is of distinct macroscopic crystallites in an amorphous matrix. An alternative stress calculator includes the crystallinity level in the equation, which is more general than Equation 7.2 although still imperfect:

$$\tau = (1-\alpha)\tau_a + \alpha\tau_c,$$ \hspace{1cm} (7.3)

where \( \alpha \) is the relative crystallinity (different from absolute crystallinity), defined as

$$\alpha = \frac{\text{crystallized volume}}{\text{total crystallizable volume}}, \text{ and ranges from 0 to 1.}$$ \hspace{1cm} (7.4)

The crystallization kinetics is based on Nakamura equation, which allows for variable temperature:

$$\alpha(t) = 1 - \exp \left[ -\left\{ \int_0^T K(T(s)) ds \right\}^n \right], \text{ where}$$ \hspace{1cm} (7.5)

\( \alpha(t) = \) relative crystallinity at time \( t \)

\( K(T(s)) = \) crystallization kinetic constant as a function of temperature \( T \)

\( n = \) empirical constant
Many crystallization experiments, as is also the case in this thesis, monitor the enhancement of viscosity. According to Tanner (2003), this can be described as a function of three parameters, of which crystallization kinetics is one of them:

\[
\frac{\eta}{\eta_0} = f\left(\frac{\phi}{\phi_m}, \text{geometry, size distribution}\right)
\]  

(7.6)

The first parameter is ratio of the volume fraction of the particles \(\phi\) to the maximum possible volume fraction \(\phi_m\), analogous to the relative crystallinity \(\alpha\). Geometry and size distribution can also be included although they normally do not exert a large influence on the final form of the equation.

For the continuous shearing at low shear rates, Tanner (2003) discusses two possible parameters by which the increase in crystallinity can be attributed to: shear rate and shear strain.

For the first case, the Nakamura crystallization kinetic constant takes the form:

\[
K = K_0(T)F_d(\dot{\gamma})
\]  

(7.7)

where \(F_d\) is the dependence of crystallization kinetics on shear rate. The crystallinity is then calculated as follows:

\[
\alpha = 1 - \exp\left[-F_d(\dot{\gamma})\left(\frac{t}{10^4}\right)^{3.1}\right]  
\]  

(7.8)

By fitting this model to the experimental results of Wassner and Maier (2000) for sheared polypropylene (PP), the following relationship is obtained:

\[
F_d(\dot{\gamma}) = 1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{1.35},
\]  

(7.9)

where \(\dot{\gamma}_c\), the critical shear rate for the transition from quiescent to shear-induced crystallization, was found to be 0.00112 s\(^{-1}\). However, this model does not fit the experimental data very well, since it predicts \(\eta/\eta_0\) curves of the same shape for every shear rate, while experiment shows that for the quiescent condition, the curve has a notably different shape.
In the second case, shear strain is considered as the important determinant for crystallization and the Nakamura constant is described as:

\[ K = K_0(T) \left( 1 + a[\dot{\gamma}]^m \right) \]  

(7.10)

where \( a \) and \( m \) are constants.

The crystallinity is calculated as follows:

\[ \alpha(t) = 1 - \exp \left( - \left( K_0 t + \frac{K_0 a[\dot{\gamma}]^m t^{m+1}}{m+1} \right)^n \right) \]  

(7.11)

By assuming this function, the form of the curves is different for the quiescent and for the shear-induced cases, in accordance with the experiments (Wassner and Maier, 2000). This suggests that shear strain is the more important determinant of increasing crystallinity as compared to shear rate, although contributions from other parameters such as shear stress or normal stress are also possible.

So far, only low shear rates are considered (the experimental data from Wassner and Maier (2000) only tested shear rates up to 0.16 s\(^{-1}\)). For extension into high shear rate region, it is likely that non-linear effects need to be incorporated into the model, which is a formidable task. It is also important to note that for the model to work, the crystallizing system must be suspension-like (SL), which is the case for PP, as shown by Boutahar et al. (1998). For other polymers, this assumption must be checked first. Lastly, experimental data on elongation-induced crystallization can also be compared to the model and this will probably cast some light on other parameters determining the crystallization kinetics.

### 8.2.4 Dumbbell model

The model proposed by Zheng and Kennedy (2004) is in principle similar to those forwarded by Doufas et al. (1999) and Tanner (2002), in which the crystallizing system is seen as a suspension of semicrystalline entities growing in an amorphous matrix. The difference is that in their case the physical properties of the amorphous phase are kept constant, so the physical properties of the suspension depend only on the semicrystalline
phase. To describe the chain conformation and orientation evolution of the amorphous phase the FENE-P (Finite Extensible Nonlinear Elastic model with a Peterlin closure approximation) dumbbell model is used, whereas the semicrystalline phase is modeled as rigid dumbbells.

The simple additive rule (Equation 7.3) was used as the stress calculator. For the amorphous phase contribution, the equation is given as:

$$\tau_a = 2c \frac{\partial(\Delta F_f)}{\partial c} = n_0 k_B T \left[ \left(1 - \frac{tr(c)}{b} \right)^{-1} c - I \right],$$  \hspace{1cm} (7.12)

where $\Delta F_f$ is the flow-induced change of free energy for a system of elastic dumbbells (Booij, 1984), $n_0$ the number density of the molecules, $k_B$ the Boltzmann constant, $T$ the temperature, $b$ the dimensionless parameter of the nonlinear spring, $c$ the dimensionless conformation tensor, and $I$ the unit tensor. The relaxation time of the amorphous fluid is incorporated in the constitutive equation for the tensor $c$ as follows:

$$\lambda_a \frac{\Delta c}{\Delta t} + \left(1 - \frac{tr(c)}{b} \right)^{-1} c = I,$$ \hspace{1cm} and

$$\lambda_a = \frac{\zeta}{4H},$$  \hspace{1cm} (7.13)

Where $\zeta$ is the friction coefficient and $H$ the spring elastic constant. An Arrhenius-type dependence is assumed for $\lambda_a$.

As for the semicrystalline stress contribution, the equation is as follows:

$$\tau_a = \mu(\alpha) \left[ 3\langle uu \rangle - I + 6\lambda_c \mathbf{D} : \langle uuuu \rangle \right],$$ with

$$\lambda_c = \zeta R^2 / 12 k_B T,$$ \hspace{1cm} (7.16)

$$\mu(\alpha) = \frac{\eta_a / \lambda_a}{1 - \alpha / A},$$ \hspace{1cm} (7.17)

where $\lambda_c$ is the time constant of the rigid dumbbell, $R$ the distance between two beads on the dumbbell, $\mu$ the melt shear modulus, $\mathbf{D}$ the rate of deformation tensor, $\langle uu \rangle$ the second-order orientation tensor, and $\langle uuuu \rangle$ the closure approximation.
The viscosity enhancement (the special form of Equation 7.6) is modeled as follows:

\[
\frac{\eta}{\eta_a} = 1 + \frac{(\alpha / A)^\beta}{(1 - \alpha / A)^\beta_1}, \quad \alpha < A, \quad (7.18)
\]

where \(\eta_a\) is the viscosity of the amorphous phase, \(\alpha\) is relative crystallinity as defined in Equation 7.4, \(A\) is geometrical parameter (taken as 0.44 for rough compact crystallites), and \(\beta\) and \(\beta_1\) are empirical parameters. The limit \(\alpha < A\) was imposed because beyond this limit the viscosity reaches infinity.

The Avrami approach is used to obtain the crystallization kinetics, with the fictive volume fraction of “phantom crystals” \(\alpha_f\) (i.e. discounting impingement effects) expressed as:

\[
\alpha_f = C_m \int_0^t \tilde{N}(s) \left[ \int G(u)du \right]^m ds, \quad (7.19)
\]

Where \(\tilde{N}\) is the nucleation rate, \(G\) is the growth rate, \(C_m\) is a shape factor (taken to be \(4\pi/3\)), and \(m\) is the Avrami index. As is generally observed, the main effect of flow is to increase the nucleation rate and not growth. Therefore, the total nuclei are the sum of quiescent and flow-activated nuclei:

\[
N = N_0 + N_f, \quad (7.20)
\]

and the flow-induced nucleation rate is:

\[
\dot{N}_f + \frac{1}{\lambda_f} N_f = f, \quad (7.21)
\]

where \(\lambda_f\) is as defined in Equation 7.1. In fact, Equation 7.21 is the general form of Equation 7.1, where \(f\) is the flow contribution function. In the case of Eder and Janeschitz-Kriegl (1997), \(f = (\dot{\gamma} / \dot{\gamma}_n)^{2} g_n\). Zheng and Kennedy (2004) proposed to use the function adopted by Coppola et al. (2001) in their microrheological model (see Section 7.2.5, Equation 7.22), which in turn is based on the theories of Lauritzen and Hofmann (1960) and Ziabicki (1996).

The developed model was compared with experimental data on an isotactic PP. Two adjustable parameters are identified: the nonlinear spring parameter \(b\) (Equation 7.13) and
the non-affine parameter $\xi$ (implicit in Equation 7.15). The parameters $\beta_1$ and $\beta$ in Equation 7.18 must also be obtained by fitting to experimental data. Only simulations for post-shear crystallization effects were conducted, and the results show the following trends:

1. Both shear rate and shearing time enhance crystallization rate, but the combination of high shear rates with short shearing times are the most effective.
2. When shearing is stopped, the number of activated nuclei per unit volume is kept constant or relaxes according to the relaxation time, instead of instantaneously reduced to the number corresponding to quiescent condition.
3. The rheology of the system is greatly affected by even a small amount of crystallinity, as can be seen from the strong increase in shear viscosity.

These can be seen in Figures 7.2, 7.3, and 7.4.

![Figure 7.2 Crystallization kinetics of i-PP at 140 °C at several combinations of shear rates and shearing times (same total shear $\gamma = 500$) (Zheng and Kennedy, 2004).](image-url)
Figure 7.3  The number of activated nuclei per unit volume for i-PP at 140 °C, sheared at different shear rates and with different shearing times (Zheng and Kennedy, 2004).

Figure 7.4  Variation of normalized shear viscosity with relative crystallinity, from Zheng and Kennedy (2004) compared with Pantani et al. (2001).

These qualitative trends agree with the experimental data for the above mentioned PP. However, because of the large number of parameters involved in the equations, some
material data might be difficult to obtain for other samples and the resulting trends could also be different. Therefore, the model should be checked for other samples, as well as for the cases of continuous shear and elongation-induced crystallization. As later shown by Tanner and Qi (2005) in their comparison of several FIC models, the dumbbell model gives only a moderate agreement when applied to continuous shear.

8.2.5 Microrheological model

Similar to the dumbbell model above, the approach employed by Coppola et al. (2001) is microrheological, i.e. the polymeric liquid is described on a molecular basis. Flow is considered to increase the nucleation rate by increasing the free energy of the liquid phase, \( \Delta G_f \).

The nucleation rate follows the proposal by Lauritzen and Hoffman (1960), given as:

\[
\hat{N} = Ck_B T \Delta G \exp \left( - \frac{E_a}{k_B T} \right) \exp \left[ - \frac{K_n}{T (\Delta G)^\alpha} \right],
\]  

(7.22)

where \( C \) is a constant comprising energetic and geometrical factors, \( k_B \) the Boltzmann constant, \( T \) the temperature, \( \Delta G \) the volumetric free energy difference between liquid and crystalline phase, \( E_a \) the activation energy of the supercooled liquid nucleus interface, and \( K_n \) a constant comprising energetic and geometrical factors for the crystalline nucleus.

The free energy difference is assumed as the sum of the quiescent and flow-induced contributions:

\[
\Delta G = \Delta G_q + \Delta G_f
\]

(7.23)

For the free energy difference under quiescent conditions:

\[
\Delta G_q = \Delta H_0 \left( 1 - \frac{T}{T_m} \right),
\]

(7.24)

where \( \Delta H_0 \) is the latent heat of crystallization and \( T_m \) the equilibrium melting temperature.
For the free energy difference under flow, the DE-IAA (Doi-Edwards with Independent Alignment Approximation) model is used. The IAA assumption reduces the mathematical complexity of the DE model and was developed by Marrucci and Grizzuti (1983). The equation takes the form:

\[
\Delta G_f = 3ck_bT \int_{-\infty}^{t} \mu(t,t')A[E(t,t')]dt',
\]

(7.25)

where \( c \) is the volumetric concentration of primitive chain segments, \( \mu \) the DE memory function, and \( E(t,t') \) the deformation history tensor between times \( t' \) and \( t \). The expression for \( \mu \) is:

\[
\mu(t,t') = \frac{8}{\pi^2} \sum_{p \text{ odd}} \frac{1}{p^2} \exp\left(-\frac{p^2(t-t')}{T_d}\right),
\]

(7.26)

where \( p \) is an integer and \( T_d \) the disengagement time.

For continuous flow either in shear or uniaxial elongation, Equation 7.25 is modified into:

\[
\Delta G_f = 3ck_bT \int_{0}^{\infty} \mu(z)A[De z]dz,
\]

(7.27)

where \( De \) is the Deborah number, and the function \( A \) is obtained from the DE-IAA model and depends on the type of flow. For shear:

\[
A(x) = \frac{1}{2} \ln \left(1 + x^2 \xi^2 + \sqrt{\xi^4 (x^4 + 4x^2) - 2x^2 \xi^2 + 1}\right) d\xi
\]

(7.28)

where \( \xi \) is the strain parameter, and for uniaxial elongation:

\[
A(x) = x + \tan^{-1}\left(\sqrt{e^{3x} - 1}\right) - 1
\]

(7.29)

Equation 7.27 reduces to more simple forms relating \( \Delta G_f \) to \( De \) for the limiting cases of low and high Deborah numbers (Coppola et al., 2001).

In Figure 7.5, the variation of the dimensionless free energy change (\( \Delta G_f/3ck_bT \)) with \( De \) for the case of shear flow is plotted, comparing the predictions from DE-IAA model, LE (linear elastic) dumbbell model, and the FENE-P dumbbell model. The DE-IAA model
predicts the least increase of free energy change with De. For the elongation flow, the increase is greater, as expected. This can be seen in Figure 7.6.

![Figure 7.5](image)

**Figure 7.5** Dimensionless free energy change as a function of De for continuous shear. 
(■ = LE dumbbell, ∆ = FENE-P dumbbell, ● = DE-IAA) (Coppola et al., 2001).

![Figure 7.6](image)

**Figure 7.6** Dimensionless free energy change as a function of De using the DE-IAA model for: ● = shear flow, and ■ = uniaxial elongation flow. Dashed lines are the limiting predictions for high De (Coppola et al., 2001).

Figure 7.7 plots the variation of dimensionless induction time Θ (instead of ΔG) with De for shear and uniaxial elongation flows. Also in this case, a larger reduction in induction time is observed for the elongation flow as compared to shear flow, with the difference reaching more than two orders of magnitude at some points. Apparently, in the limit of
high De’s, the slopes of the curves flatten because in this region it is predicted that the maximum extension of the polymer chains is achieved.

Coppola et al. (2001) show that the reduction in induction time predicted by the DE-IAA model agree well with the experimental data from Lagasse and Maxwell (1976) for polypropylene and polyethylene samples. On the other hand, the LE dumbbell model overestimates this reduction. From their own experiments on isotactic polypropylene, Aciero et al. (2002) also demonstrate a very good agreement between the induction times obtained from the model and experimental data (Figure 7.8). However, because of the low shear rates applied ($10^{-4}$ s$^{-1}$ to 1 s$^{-1}$), the existence of the second plateau at high De’s is not evident. As the temperature increases and approaches the equilibrium melting temperature $T_m$, it is predicted that there is a greater effect of flow on the acceleration of the nucleation kinetics.

Compared to the other models, the DE-IAA model is quite straightforward to use and it is also applicable to shear flow or uniaxial elongational flow. In principle, no adjustable parameter is introduced in the model, which increases its attractiveness. However, the disengagement or reptation time $T_d$ is not well-defined and might be difficult to obtain from experiments. In effect, $T_d$ might be viewed as an adjustable parameter that depends
strongly on the molecular weight $M_w$. It is also a weakness of this model that only a single relaxation time is used, therefore for a polydisperse sample the polymer behavior will not be correctly described.

Figure 7.8 Dimensionless induction time as a function of shear rate for an isotactic polypropylene at $140^\circ C (T_d = 40 \text{ s})$. The points are experimental data, and the line is prediction from DE-IAA model (Acierno et al., 2002).

8.2.6 Recoverable strain-based model

In the model proposed by Zuidema (2000) and confirmed by Peters et al. (2002), the controlling parameter for FIC is the recoverable strain (expressed by the elastic Finger tensor) with the highest relaxation time. The reason is that in a multi-modal approach, the mode with the highest relaxation time will contribute the most. Recoverable strain is a measure to viscoelastic stress, which exists because of molecular orientation and stretch. Consequently, it is necessary to first select the appropriate viscoelastic model.

The following constitutive equations are used to

$$\sigma = G_0 B_e,$$  \hspace{1cm} \text{(7.30)}

$$\tau = G_0 (B_e - I),$$  \hspace{1cm} \text{(7.31)}

where $\sigma$ is the Cauchy stress tensor, $B_e$ the recoverable strain tensor, $I$ the unit tensor, $G_0$ the elastic modulus, and $\tau$ the extra stress.
In the multi-mode form:

\[ \sigma = -pI + \sum_{i}^{n} \tau_{i}, \quad (7.32) \]

where \( p \) is the hydrostatic pressure.

The Leonov and XPP models were compared to calculate the stresses and the relaxation times, of which the latter was considered better to fit the polymer behavior in elongation. Therefore, Leonov model was applied for shear flow whereas XPP model was applied for extensional flow. The viscoelastic stress terms were replaced by \( B_{e} \), in accordance with the proposed model.

For the crystallization kinetics, Schneider’s set of differential equations (Schneider et al., 1988) were modified to account for the flow effects:

\[
\begin{align*}
\dot{\psi}_{3} + \frac{1}{\tau_{n}}\psi_{3} &= 8\pi J_{2} g_{n} \quad \text{‘rate’} \\
\dot{\psi}_{2} + \frac{1}{\tau_{l}}\psi_{2} &= \psi_{3}J_{2} \frac{g_{l}}{g_{n}} \quad \text{‘length’} \\
\dot{\psi}_{1} &= G\psi_{2} \quad \text{‘surface’} \\
\dot{\psi}_{0} &= G\psi_{1} \quad \text{‘volume’}
\end{align*}
\]  

(7.33)

where \( \psi \) is the parameter that can represent rate, length, surface, or volume, \( G \) the crystal growth rate, \( g_{l} \) the parameter for the axial shish growth, \( g_{n} \) the parameter for the nucleation rate, \( \tau_{l} \) the relaxation time for the shish, \( \tau_{n} \) the relaxation time for nuclei formation, and \( J_{2} \) the second invariant of the deviatoric part of the recoverable strain tensor, defined as:

\[ J_{2}(B_{e}^{d}) = \frac{1}{2} B_{e}^{d} \cdot B_{e}^{d} \quad (7.34) \]

where \( d \) signifies the deviatoric part.

The Finite Element Methods (FEM) was used to analyze the interplay between rheology and FIC. So far, a linear relationship was considered for the coupling, however in reality it is more complex, especially for the high flow rates considered in the simulations. A good agreement was obtained between the numerical and experimental results for the
case of shear, while for elongation the agreement was only qualitative (Peters et al., 2002). The model is mainly useful to predict the spatial distribution of the crystalline structure in an injection molded products, and more research needs to be done to link this to the final product properties (e.g. density distribution and residual stresses).

8.2.7 Configurational entropy based model

In this case, the rheology of the polymer melt is described by a thermodynamically consistent reptation model (TCR), originally developed by Öttinger (1999) for monodisperse entangled linear polymer systems. The application is extended to polydisperse systems in van Meerveld (2005). The TCR is a variation of the Doi-Edwards “tube” and reptation model (1986) incorporating the Convective Constraint Release (CCR) mechanism proposed by Marrucci (1996). The constraint release (CR) takes into account how the removal of tube segments (which represents entanglements) influences the relaxation of the contour path, whereas the CCR additionally describes the number of constraints lost due to the retraction of the chains forming the tube.

The TCR approach is extensively based on the molecular theory and it is important to describe the evolution of the polymer chain contour path by a configuration distribution function \( f(u, s, r, t) \). Here, \( u \) is the unit orientation vector and \( s \) the curvilinear coordinate associated with the position of polymer segment along the contour path. The function is given by the Fokker-Planck equation for a monodisperse sample:

\[
\frac{D f}{D t} = -\frac{\partial}{\partial u} \cdot \left[ \left( I - \frac{uu}{|u|^2} \right) \cdot \kappa \cdot u f \right] + \frac{1}{\tau_d \lambda^2} \frac{\partial^2 f}{\partial s^2} + \frac{\partial}{\partial s} \left( s - \frac{1}{2} \frac{\dot{\lambda}_{\text{dissip}}}{\lambda} f - \frac{\dot{\lambda}_{\text{dissip}}}{\lambda} f + \frac{\partial}{\partial u} \cdot D \left( I - \frac{uu}{|u|^2} \right) \cdot \frac{\partial}{\partial u} f \right).
\]

(7.35)

where:
\( I \) = unit tensor,
\( \kappa \) = the transpose of the velocity gradient,
\( \tau_d \) = reptation time,
\( \dot{\lambda}_{\text{dissip}} \) = dissipation rate.
\[ \dot{\lambda}_{\text{dissip}} = \text{expression for chain retraction dynamics,} \]

\[ \lambda = \text{stretch ratio of the current length contour path (} L \text{) to the equilibrium value (} L_0 \text{),} \]

\[ D = \text{constraint release parameter.} \]

The \( \dot{\lambda}_{\text{dissip}} \) is related to the \( \lambda \) and \( \lambda_{\text{max}} \), the latter being the maximum stretch ratio (dependent only on the chemical nature of the polymer).

Figure 7.9  (a) Illustration of the contour path of a chain, with the orientation vector \( u \) of a segment on the path and the average chain stretch \( l \).  (b) The contour path and Kuhn chain segments at equilibrium, (c) for an oriented but non-stretched contour path, and (d) for an oriented and stretched contour path.  (van Meerveld et al., 2004).

The above model is then incorporated in a non-equilibrium thermodynamic GENERIC (General Equation for Non-Equilibrium Reversible Irreversible Coupling) framework (Öttinger, 1999) before applied to a non-isothermal FIC case. A set of rate equations is used to separate nucleation and growth stages, in contrast to the Nakamura equation used by Doufas et al. (2000). Also, the governing parameter for nucleation here is the change in the configuration of amorphous chains, focusing on the high molecular weight tail of the molecular weight distribution, since this part contributes the most to FIC. In the model, flow-induced crystallization is predicted only when the reduction of the end-to-end distance of the amorphous part of the chain is larger compared to the increase of the
relative extension of the chain under flow (van Meerveld, 2005). Consequently, the onset of orientation and stretching is characterized by means of Deborah numbers based on the reptation and stretching time of the high molecular weight chains.

The proposed model works reasonably well for fiber spinning simulations of nylon 66 and PET, giving quantitative agreement with the measured velocity and temperature profiles. Improvements might be introduced by considering a more refined description of chain dynamics, for example by the Rouse model (van Meerveld, 2005). However, the treatment might prove to be bulky for highly polydisperse samples, as Equation 7.35 needs to be extended according to the assumed number of modes, each representing a molecular weight. The semi-phenomenological nature of the model also makes it difficult to obtain the necessary experimental data. Finally, the application of the model in other processes such as injection molding needs to be tested.

8.2.8 Comparison of the models

The FIC models described above represent quite well the current spectrum, but they are certainly not exclusive and there are more variations not included here. In deciding the applicability of these models for a particular situation, the five factors below must be considered:

- Critical parameter for crystallization.
  As identified by Tanner and Qi (2005), there are seven parameters, from which one can select as the determinant for flow-induced crystallization (with the main effect on nucleation rate): shear rate, shear strain, stress, normal stress difference, recoverable shear strain, free energy of dumbbells, and work input. It is still debatable as to which one exerts the strongest influence and under what conditions. More experimental data are required for the generalization of these models.

- Isothermal/non-isothermal process.
  Some of the models are only developed for isothermal condition, for example the continuum model (Doufas et al., 1999) and the microrheological model (Coppola

- **“Micro-” vs. “macro-” rheology.**
A microrheology approach means that the model is based on the molecular motion of the polymer chains and how it is affected by the crystallization. Consequently, the choice of viscoelastic theory like the XPP, Leonov, and the PTT theories determines the quality of the model. This is the case for the models proposed by Zuidema (2000), Coppola et al. (2001), Tanner (2003), and Zheng and Kennedy (2004). Other researchers opt to derive relationships from more global phenomena such as observed in rheological or rheo-optical experiments, for example Eder and Janeschitz-Kriegl (1997) and Doufas et al. (1999).

- **Material.**
Many of the models were based on the experimental data for i-PP, for which the material properties are also widely available. However, i-PP has certain attributes that are quite different to other polymers, for example its mesomorphic ($\gamma$) phase. Tanner (2003) also warns that the suspension-like (SL) assumption that is valid for PP might not be applicable for other polymers. Therefore, again the models must be tested against a wider range of materials.

- **Application.**
The experimental methods on which a certain model is based or tested are also important to decide for which specific type of flow (elongation vs. shear) and condition (post-flow vs. continuous flow) the model can be applied. For example, Doufas et al. (1999) developed the model particularly for fiber spinning, while in the cases of Eder and Janeschitz-Kriegl (1997) and Zheng and Kennedy (2004) the intended application is for injection molding (post-shearing condition). Several models claim to be suitable for both shear and elongation (Coppola et al. (2001), Zuidema (2000)), however because of lack of data in elongation-induced crystallization their applicability is still to be assessed.
7.3 Agreement with Experimental Data

In this section the experimental data obtained for PB-1 in shear and elongation flows are compared with the prediction from one of the FIC models, namely the microrheological modeling proposed by Coppola et al. (2001). The reason to choose this model is that it is relatively straightforward to use and practically only one adjustable parameter is involved (the disengagement time $T_d$). Furthermore, the equations for shear and elongation are already given for this model. The data from BR200 will be used, because it is the only sample tested both in shear- and elongation-induced crystallization experiments. As mentioned in the previous chapter, with the other samples having lower molecular weights than BR200, EIC experiments were not successful because they sagged during the annealing stage.

In Table 7.1, the material properties of BR200 and other constants used in the calculation are listed:

<table>
<thead>
<tr>
<th>Variable</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt density</td>
<td>$\rho$</td>
<td>914</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Molecular weight for entanglements</td>
<td>$M_e$</td>
<td>18 400</td>
<td>g/mol</td>
</tr>
<tr>
<td>Molecular weight of repeat unit</td>
<td>$M_{\text{unit}}$</td>
<td>56.11</td>
<td>g/mol</td>
</tr>
<tr>
<td>Weight-average molecular weight</td>
<td>$M_w$</td>
<td>762 000</td>
<td>g/mol</td>
</tr>
<tr>
<td>Entanglement density</td>
<td>$c$</td>
<td>$2.99 \times 10^{-25}$</td>
<td>/m$^3$</td>
</tr>
<tr>
<td>Equilibrium melting temperature</td>
<td>$T_m^0$</td>
<td>411</td>
<td>K</td>
</tr>
<tr>
<td>Experimental temperature (isothermal)</td>
<td>$T$</td>
<td>376</td>
<td>K</td>
</tr>
<tr>
<td>Latent heat of crystallization</td>
<td>$\Delta H_0$</td>
<td>34.8</td>
<td>J/g</td>
</tr>
<tr>
<td>Longest relaxation time @ 103 °C</td>
<td>$\Lambda$</td>
<td>530</td>
<td>s</td>
</tr>
<tr>
<td>Disengagement time @ 103 °C</td>
<td>$T_d$</td>
<td>50</td>
<td>s</td>
</tr>
<tr>
<td>Energetic / geometrical constant</td>
<td>$K_n$</td>
<td>$1.0 \times 10^{10}$</td>
<td>(J/m$^3$)$^n$</td>
</tr>
<tr>
<td>Exponent of homogeneous nucleation</td>
<td>$n$</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Avogadro number</td>
<td>$N$</td>
<td>$6.22 \times 10^{23}$</td>
<td>/mol</td>
</tr>
<tr>
<td>Boltzmann constant</td>
<td>$K$</td>
<td>$1.38 \times 10^{-23}$</td>
<td>J/K</td>
</tr>
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</table>
The quiescent free energy change, $\Delta G_q$, is calculated as follows:

$$\Delta G_q = \Delta H_q \left(1 - \frac{T}{T_m}\right)$$  \hspace{1cm} (7.36)

Using the values in Table 7.1, $\Delta G_q = 2.7 \times 10^6 \text{ J/m}^3$.

The next step is to calculate the $\Delta G_f/3ckT$ term (Equation 7.27), which varies with the Deborah number. The relationship is plotted in Figure 7.9. The result compares well with Figure 7.6, in which a greater gap between the change in free energy term in elongation and in shear is seen as De increases. Here, the difference is already more than one decade at De = 10.

![Figure 7.10](image)

**Figure 7.10** The variation of change of free energy due to flow (as predicted from the microrheological model) with De for BR200 in shear and elongation ($T = 103 ^\circ C$).
Based on the plot in Figure 7.9, it is also expected that elongation flow will induce a more dramatic reduction in induction time. This is shown in Figure 7.10, comparing the prediction from microrheological model with actual experimental data obtained for BR200 at 103 °C.

![Graph showing comparison between prediction and experiment](image)

**Figure 7.11** Comparison between the prediction of dimensionless induction time (normalized to the quiescent induction time) from microrheological model and experimental data for BR200 at 103 °C, for shear and elongation.

It can be seen that at the beginning and up to flow rate of 10 s⁻¹, the qualitative agreement between model and data is quite good. A plateau is predicted at first, which indicates the quasi-quiescent region. The plateau for elongational flow is much shorter than that for shear flow. At higher De’s, however, the model predicts a second plateau, which is not seen in the experimental data. In fact, the onset time keeps decreasing until the largest flow rate attempted. The most probable reason why the model fails in this region is because only one relaxation time ($T_d$) is included, whereas BR200 has a very broad molecular weight distribution ($M_w/M_n = 19.6$). A sample which has a narrow distribution and yet high molecular weight to withstand the annealing period (especially in elongation experiments) was unfortunately not available. Still, Figure 7.10 presents an interesting comparison between crystallization behavior in shear and elongational flows. While this research is concerned mainly with experimental data and how to extend the range to higher flow rates, the results can act as a trigger for further studies to improve the FIC simulations.
8. CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions
The flow-induced crystallization behavior of PB-1 under shear (SIC) and under uniaxial elongation (EIC) has been covered in this project. Several experimental methods, mainly utilizing rheological principles, were employed to monitor the crystallization progress. Crystallization occurs and is monitored during the flow, as opposed to post-flow. All the crystallization experiments were done under isothermal condition, after the sample had been subjected to a well-defined temperature protocol to erase the thermal and flow histories. A certain parameter (viscosity or pressure, depending on the method) was selected to monitor the crystallization progress, from which the crystallization onset time ($t_{on}$) was defined.

Firstly, experiments under quiescent/quasi-quiescent conditions were performed as a means to assess the crystallization onset time definition and measurement. To this end, the sample was subjected to three different types of treatment: Small Amplitude Oscillatory Shear (SAOS), continuous shear, and constant stress. The controlling parameter in each case was kept small to avoid flow-induced crystallization. A very good agreement in $t_{on}$ was found for all three methods, showing the robustness of the $t_{on}$ quantity. This is an important validation, because for the SIC experiments the continuous shear method was used. Furthermore, $t_{on}$ was compared with another quantity pertinent to quiescent crystallization, namely the gel time ($t_{gel}$). The gel time was detected earlier than $t_{on}$, when the growing spherulites act as physical crosslinking points in the melt, whereas $t_{on}$ mainly reflects the filler effects of crystallites. However, the measurement of $t_{gel}$ has to be done in the flow region and therefore the selection of angular frequency range decides the result. This requirement becomes particularly difficult to fulfil for high molecular weight samples. For this reason, $t_{on}$ fares better as a quantity to measure quiescent crystallization.

As the shear rate is increased, one enters the shear-induced crystallization region. In the project, two experimental methods by which high shear rate range can be accessed have been successfully established, employing capillary rheometer and concentric cylinder
rheometer. By combining the results with those obtained from the standard ARES rheometer, experimental data for shear rates ranging from $10^{-4}$ s$^{-1}$ to 500 s$^{-1}$ were obtained. In this case a good agreement between the three methods was also found, although the onset times measured from the capillary rheometer came later than those from the other two methods. This is reasonable because a different parameter (pressure instead of viscosity) was used, and more work needs to be done to link the two together. As expected, the onset time data show a plateau-and-slope trend, which can be fitted with a Cross function. In the limit of high shear rates, a slope of -1 was observed.

The temperature dependence of the onset time is reduced for higher shear rates, indicating that the orientation and/or stretching of the polymer chains play a larger part in this region. A normalization method was proposed, by which the onset time data obtained at different degrees of undercooling collapse into one curve (the T-invariant curve). The purpose of introducing this method is to establish a comparison tool for the SIC behavior of different PB-1 samples. Additionally, by validating the existence of T-invariant curve, the number of experiments required for each new sample can be reduced.

For EIC experiments, a recently commercialized device called the Extensional Viscosity Fixture (EVF) was utilized. Since the device is initially made for elongational viscosity measurements in melt state, a protocol for conducting EIC experiments had to be established first. The experiments covered a strain rate range from $10^{-4}$ s$^{-1}$ to 10 s$^{-1}$. In the limit of small strain rates, it is shown that a quasi-quiescent condition having the same onset time as in shear was achieved. In the EIC region, the reduction in onset time was greater than that observed in SIC, comparing the same flow rates. While this fact is already widely known, in this study the onset time data for SIC and EIC are presented together for the first time in the same flow rate range, having common values at quasi-quiescent condition. The difference between the onset times in SIC and EIC already amounts to more than one decade for a flow rate of 10 s$^{-1}$.

The second main goal of this project is to investigate the effects of molecular parameters on flow-induced crystallization. Five molecular parameters were considered: molecular
weight, molecular weight distribution, isotacticity, presence and type of nucleating agents, and copolymer (ethylene) content. In the case of quiescent crystallization, it was shown that molecular weight and molecular weight distribution do not have any effects on the onset time, measured at the same degree of undercooling. A decrease in isotacticity reduces the melting point but does not affect the temperature dependence of quiescent crystallization kinetics. One of the two nucleating agents tested (EBS) brings about a 20 times increase in the kinetics, while the other nucleant (HDPE) does not have much effects. Lastly, the copolymers show different temperature dependences compared to the homopolymers, which suggests a crystallization mechanism that generates less perfect crystals.

In shear-induced crystallization, the length of the polymer chains plays a large role in promoting crystallization, as seen from the shift to the left (shorter onset times) of the T-invariant curves as the molecular weight increases and molecular weight distribution becomes broader. A common slope of -1 is maintained for these samples. Isotacticity was observed to have only a small effect on the onset time, especially as the shear rate increases. As for the nucleating agent, again only the EBS was found to have a significant effect on the absolute crystallization kinetics, although when comparing the T-invariant curves, the same gain in crystallization kinetics as for the non-nucleated sample is seen. This trend was also observed for the copolymer samples.

Finally, crystallization modeling is briefly covered in this thesis and a few FIC models are discussed. The experimental data were compared with prediction from microrheological modeling proposed by Coppola et al. (2001), which can be used either for shear or for uniaxial elongation. A reasonably good agreement is seen at small flow rates, but as the flow rate is increased, the model predicts a second plateau whereas the onset time data from the experiment keep decreasing. One possible reason for this discrepancy is that the model only uses a single relaxation time, whereas the actual sample (BR200) has a broad distribution and therefore a spectrum of relaxation times. For a more detailed modeling of the experimental data obtained in this study, more in-depth analysis should be carried out.
8.2 Recommendations

The project covers several important topics in flow-induced crystallization research and provides a significant ground for further research work. While a significant extension into high shear rate range has been achieved here (close to the shear rates encountered in extrusion), it is still far from the magnitudes common for shear-intensive processes like injection moulding. Other techniques should be developed to access even higher shear rates under well-defined conditions.

The availability of samples with well-defined molecular parameters is also important for further research. In this study, commercial samples were used and it was not possible to clearly differentiate the effects of molecular weight from molecular weight distribution on FIC, as both parameters vary in the same direction for the given array of samples. To do this, one needs a sample with a high molecular weight but narrow distribution, for example. Other polymers can also be tested using the experimental methods developed here.

The results obtained in this project are mainly empirical and a more detailed comparison with theoretical models is required. The EIC onset time data are especially valuable in this respect, because so far most of the models are compared only with SIC data. More samples that are suitable for the EIC experiments need to be produced to add more experimental data and also to investigate the effects of molecular parameters for this flow type.
LIST OF REFERENCES


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developments: chain retraction; identification of molecular weight fractions in mixture”, *Polymer*, v.21, p.1295-1298.


APPENDIX A

PRODUCT DESCRIPTION AND MATERIAL SAFETY DATA SHEETS FOR PB-1 SAMPLES
Polybutene-1
PB 0110

Polybutene-1 grade PB 0110 is a semi-crystalline nucleated homopolymer, which can be used where creep and environmental stress crack resistance is important. It has excellent retention of its physical properties at elevated temperature (up to 90 °C) and is the lowest melt flow resin available in the PB-1 product family. PB 0110 is primarily converted by extrusion or blow molding. It can also be injection molded, however there is a significant effect on properties from process induced orientation, as can be seen from the difference in properties between compression and injection molded specimens.

This polymer is highly compatible with polypropylene due to its similar molecular structure. It can be used to improve mechanical properties like impact and sealing behaviour.

It is less compatible in blends with polyethylene but it is still easily dispersible. It is used as the minor component in polyethylene film sealants for easy-opening (seal-peel) packaging applications. In combination with HDPE, it can be used for applications requiring autoclave treatment.

PB 0110 is natural in color and contains a high level of heat stabilisers, but is not UV stabilized.

PB 0110 meets FDA requirements for direct food contact under regulation 21CFR 177.1570.

### TYPICAL PROPERTIES

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<th>VALUE(a)</th>
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<tr>
<td>Notched Izod Impact (- 20 °C)</td>
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</tbody>
</table>

(a)The property values shown are based on a limited number of tests and, therefore, should not be construed as product specifications. These values may shift slightly as additional data are accumulated.

(b)ASTM test methods are the latest under the Society current procedures where applicable. Unless mentioned otherwise, specimens are prepared by injection moulding (ASTM 2146).

Issued: 02/01

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- UK: +44 1244 670 000

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**Polybutene-1**

**PB 0200**

Polybutene-1 grade *PB 0200* is a semi-crystalline homopolymer, which can be used where creep and environmental stress crack resistance and retention of properties at elevated temperature are key requirements.

This polymer is highly compatible with polypropylene due to its similar molecular structure. It can be used to improve mechanical properties like impact and sealing behaviour.

It is less compatible in blends with polyethylene but it is still easily dispersible. It is used as the minor component in polyethylene film sealants for easy-opening (seal-peel) packaging applications. In combination with HDPE, it can be used for applications requiring autoclave treatment.

*PB 0200* is natural in color and contains a low level of heat stabilizer, but is not UV stabilized.

Polybutene-1 grade *PB 0200* meets FDA requirements in 21CFR 177.1570 for food contact applications excluding cooking. For cooking, *PB 0200* can be used at a maximum thickness of 0.1 millimeter (0.004 inch).

### TYPICAL PROPERTIES

<table>
<thead>
<tr>
<th>METHOD(b)</th>
<th>UNIT</th>
<th>VALUE(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Flow Rate 190 ºC / 2.16 Kg</td>
<td>ISO 1133</td>
<td>g/10min</td>
</tr>
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<td>ISO 1133</td>
<td>g/10min</td>
</tr>
<tr>
<td>Density</td>
<td>ISO 1183/a</td>
<td>g/cm³</td>
</tr>
<tr>
<td><strong>Mechanical Properties (measured on specimens conditioned for 10 days at 20ºC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
</tr>
<tr>
<td>Tensile Strength at Break</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>ISO R527</td>
<td>%</td>
</tr>
<tr>
<td>Elongation at Break (compression moulded)</td>
<td>ASTM D638</td>
<td>%</td>
</tr>
<tr>
<td>Notched Izod Impact (Roomtemperature)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
</tr>
<tr>
<td>Notched Izod Impact (- 20 ºC)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (Tm1)</td>
<td>DSC</td>
<td>°C (ºF)</td>
</tr>
<tr>
<td>Vicat Softening point</td>
<td>ISO 306,Method A</td>
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</tr>
</tbody>
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(b) ASTM test methods are the latest under the Society current procedures where applicable. Unless mentioned otherwise, specimens are prepared by injection moulding (ASTM 2146).

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Polybutene-1
PB 0300

Polybutene-1 grade PB 0300 is a semi-crystalline homopolymer, which can be used where creep and environmental stress crack resistance, and retention of properties at elevated temperature are key requirements. It is well suited for injection molded applications, although it is not nucleated.

This polymer is highly compatible with polypropylene due to its similar molecular structure. It can be used to improve mechanical properties of polypropylene like impact and sealing behaviour.

It is less compatible in blends with polyethylene but it is still easily dispersible. It is used as the minor component in polyethylene film sealants for easy-opening (seal-peel) packaging applications. In combination with HDPE, it can be used for applications requiring autoclave treatment.

PB 0300 is natural in color and contains a low level of heat stabilizer, but is not UV stabilized.

Polybutene-1 grade PB 0300 meets FDA requirements in 21CFR 177.1570 for food contact applications excluding cooking. For cooking, PB 0300 can be used at a maximum thickness of 0.1 millimeter (0.004 inch).

### TYPICAL PROPERTIES

<table>
<thead>
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</thead>
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<td></td>
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<td>ISO 1133</td>
<td>g/10min</td>
</tr>
<tr>
<td>Melt Flow Rate 230 ºC / 2.16 Kg</td>
<td>ISO 1133</td>
<td>g/10min</td>
</tr>
<tr>
<td>Density</td>
<td>ISO 1183/a</td>
<td>g/cm³</td>
</tr>
<tr>
<td><strong>Mechanical Properties (measured on specimens conditioned for 10 days at 20 ºC)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
</tr>
<tr>
<td>Tensile Strength at Break</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>ISO R527</td>
<td>%</td>
</tr>
<tr>
<td>Elongation at Break (compression moulded)</td>
<td>ASTM D638</td>
<td>%</td>
</tr>
<tr>
<td>Notched Izod Impact (Roomtemperature)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
</tr>
<tr>
<td>Notched Izod Impact (- 20 ºC)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (Tm1)</td>
<td>DSC</td>
<td>ºC (ºF)</td>
</tr>
<tr>
<td>Vicat Softening point</td>
<td>ISO 306,Method A</td>
<td>ºC (ºF)</td>
</tr>
</tbody>
</table>

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(b) ASTM test methods are the latest under the Society current procedures where applicable. Unless mentioned otherwise, specimens are prepared by injection moulding (ASTM 2146).

Issued: 02/01
Polybutene-1
PB 0400

Polybutene-1 grade PB0400 is a semi-crystalline homopolymer, which can be used where creep and environmental stress crack resistance, elevated temperature performance are key requirements and where a high retention of induced orientation can be tolerated. An illustration of the latter behaviour can be found for elongation at break data of compression versus injection moulding specimens (see table). This difference is more pronounced compared to other polyolefins.

This polymer is highly compatible with polypropylene due to its similar molecular structure. It can be used to improve mechanical properties like impact and sealing behaviour. In blends with polyethylenes it is less compatible, but still easily dispersible. It forms a clear 2 phase structure which forms the basis of the seal peel technology for easy opening packaging applications.

PB-1 grades exhibit relative low crystallisation kinetics allowing for an excellent wetting behaviour. Together with their very shear sensitive flow behaviour it remains easy dispersible also in even more incompatible polymers like thermoplastic elastomers.

PB0400 meets FDA requirements for direct food contact under regulation 21CFR 177.1570.

**TYPICAL PHYSICAL PROPERTIES (a)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Method</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>General properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Flow Rate 190°C / 2.16 Kg</td>
<td>ISO 1133</td>
<td>g/10min</td>
<td>17</td>
</tr>
<tr>
<td>Melt Flow Rate 230°C / 2.16 Kg</td>
<td>ISO 1133</td>
<td>g/10min</td>
<td>66</td>
</tr>
<tr>
<td>Density</td>
<td>ISO 1183/a</td>
<td>g/cm³</td>
<td>0.915</td>
</tr>
<tr>
<td>Mechanical properties (conditioned 10 days @ 20°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
<td>215(31175)</td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>ISO R527</td>
<td>MPa (psi)</td>
<td>28(4060)</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>ISO R527</td>
<td>%</td>
<td>270</td>
</tr>
<tr>
<td>Elongation at break (compression moulded)</td>
<td>ASTM D638</td>
<td>%</td>
<td>380</td>
</tr>
<tr>
<td>Notched Izod Impact (Roomtemperature)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
<td>No Break</td>
</tr>
<tr>
<td>Notched Izod Impact (-20°C)</td>
<td>ISO 180, Notch A</td>
<td>kJ/m² (ft.lbf/in²)</td>
<td>9(4.28)</td>
</tr>
<tr>
<td>Thermal properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point (Tm1)</td>
<td>DSC</td>
<td>°C</td>
<td>119(246)</td>
</tr>
<tr>
<td>Vicat Softening point</td>
<td>ISO 306, Method A</td>
<td>°F</td>
<td>106(223)</td>
</tr>
</tbody>
</table>

a) Values shown are typical values and may shift within specification limits
b) All mechanical properties are determined from injection moulded specimens unless otherwise specified

07/99
Polybutene-1

PB 0800

Polybutene-1 grade **PB 0800** is an isotactic, semi-crystalline (50%) homopolymer which may be used where creep resistance, environmental stress crack resistance and elevated temperature performance are key requirements. PB 0800 is miscible with polypropylenes due to its similar molecular structure. In blends with polyethylenes it is immiscible but easily dispersible.

This grade is mainly used as a concentrate carrier and in hot melt adhesives where higher service temperatures, high strength and/or long open times are required. PB 0800 meets FDA adhesive regulation 21CFR 175.105 for indirect food contact.

<table>
<thead>
<tr>
<th>TYPICAL PHYSICAL PROPERTIES (a)</th>
<th>METHOD (b)</th>
<th>UNIT</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Flow Rate</td>
<td>ISO 1133-1981E</td>
<td>dg/min</td>
<td>200</td>
</tr>
<tr>
<td>Density</td>
<td>ASTM D1505</td>
<td>g/cm³</td>
<td>0.915</td>
</tr>
<tr>
<td><strong>Mechanical properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength at yield</td>
<td>ISO 1184-1983E</td>
<td>MPa</td>
<td>13.8</td>
</tr>
<tr>
<td>Tensile strength at break</td>
<td>ISO 1184-1983E</td>
<td>MPa</td>
<td>&gt; 22.0</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>ISO 1184-1983E</td>
<td>percent</td>
<td>&gt; 300</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>ISO 1184-1983E</td>
<td>MPa</td>
<td>241</td>
</tr>
<tr>
<td>Envir’t stress crack resistance</td>
<td>ASTM D1693</td>
<td>h</td>
<td>&gt; 15000 *</td>
</tr>
<tr>
<td><strong>Thermal properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting point range</td>
<td>D.T.A.</td>
<td>°C</td>
<td>124 – 126</td>
</tr>
<tr>
<td>Softening point (Ring &amp; Ball)</td>
<td>ASTM E28</td>
<td>°C</td>
<td>116</td>
</tr>
<tr>
<td>Britteness temperature</td>
<td>ASTM D 746</td>
<td>°C</td>
<td>- 18</td>
</tr>
</tbody>
</table>

a) Values shown are averages and not to be considered as product specifications. These values may shift slightly as more data is accumulated
b) ASTM test methods are the latest under the Society’s current procedures. All specimens are prepared by injection (ASTM 2146)

* No failure after 15000 hrs at 50°C in 10% Igepal CO630
1. PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Polybutene-1 PB 0300
PRODUCT DESCRIPTION: Polybutylene Homopolymer Pellets

MANUFACTURER
Basell USA Inc.
912 Appleton Road
Elkton, MD 21921-3920

Basell Canada Inc.
339 LaSalle Road
Corunna, Ontario
N0N 1G0
Product Stewardship: 410-996-1600

24 HR. EMERGENCY TELEPHONE NUMBERS
CHEMTREC (U.S.): (800) 424-9300
CANUTEC: (613) 996-6666

2. COMPOSITION / INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Wt.%</th>
<th>CAS#</th>
<th>EINECS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutylene</td>
<td>&gt;95</td>
<td>9003-28-5</td>
<td></td>
</tr>
<tr>
<td>Stabilizers (trade secret)</td>
<td>&lt;5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

COMMENTS: This product is not considered a hazardous material at temperatures below the melting point as determined by Basell according to the U.S. Occupational Safety and Health Act definitions and regulation, including the Hazard Communication Standard 29 CFR 1910.1200. This product is not considered a controlled substance by Basell according to Canada's WHMIS regulations. Threshold Limit Values (TLV) or Permissible Exposure Limit (PEL) values are not established. This material is not expected to cause physiologic impairment at low concentration. Until a specific TLV is adopted by ACGIH (American Conference of Governmental Hygienists), or an OSHA (Occupational Safety and Health Administration) PEL standard is issued, Basell suggests that this material be treated as a nuisance dust or particulate in accordance with the recommendations of ACGIH.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

PHYSICAL APPEARANCE: Translucent to white solid pellets

IMMEDIATE CONCERNS: Spilled material may present a slipping hazard. This product as shipped is not classified as a combustible dust; however, a combustible concentration of dust may occur if fines are suspended in air. Avoid contact with strong oxidizing agents. When working with the material at temperatures above the melting point, the material will begin to decompose producing fumes that can contain carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes and other unidentified organic compounds that come from the breakdown of the material. Adequate room and extruder ventilation should be provided to minimize exposures.
POTENTIAL HEALTH EFFECTS

**EYES:** Process vapors may irritate eyes.

**SKIN:** Exposure to molten resin may cause thermal burns.

**INGESTION:** Not Applicable

**INHALATION:** Process vapors may cause respiratory tract irritation.

SIGNs AND SYMPTOMS OF OVEREXPOSURE

**EYES:** Irritation or redness.

**SKIN:** Not Applicable

**INGESTION:** Not Applicable

**INHALATION:** Irritation of the nose, throat and respiratory tract.

**ACUTE TOXICITY:** Process vapors may cause eye and respiratory tract irritation.

**CHRONIC:** None Known

**CARCINOGENICITY:** None Known

**MUTAGENICITY:** None Known

REPRODUCTIVE TOXICITY

**REPRODUCTIVE EFFECTS:** None Known

**TERATOGENIC EFFECTS:** None Known

**MEDICAL CONDITIONS AGGRAVATED:** None Known

**ROUTES OF ENTRY:** Eye, Inhalation

**TARGET ORGAN STATEMENT:** None Known

**CANCER STATEMENT:** This product is not considered to be a carcinogen by OSHA, IARC or NTP.

**IRRITANCY:** Exposure to process vapors may cause eye and respiratory tract irritation.

**SENSITIZATION:** None Known

**WARNING CAUTION LABELS:** Burn Risk - Avoid contact with molten resin. Explosion Risk - Prevent accumulation of dust particles. Slipping Risk - Keep walking surfaces free of spilled material. Vapor Risk - Provide ventilation to avoid exposure to process vapors.

**COMMENTS HEALTH:** None

**HEALTH HAZARDS:** Process vapors may cause eye and respiratory tract irritation.

**PHYSICAL HAZARDS:** Spilled material may present a slipping hazard. Exposure to molten resin may cause thermal burns.

---

**4. FIRST AID MEASURES**

**EYES:** Flush eyes with water for 15 minutes. Get medical attention.

**SKIN:** Molten Resin: If molten material comes in contact with the skin, cool under ice water or a running stream of water. DO NOT attempt to remove the material from the skin. Removal could result in severe tissue damage. Get medical attention.

**INGESTION:** Not Applicable

**INHALATION:** Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

**ANTIDOTES:** Not Applicable
5. FIRE FIGHTING MEASURES

**AUTOIGNITION TEMPERATURE:** Not Determined

**EXTINGUISHING MEDIA:** Use foam, carbon dioxide, or water spray when fighting fires involving this material.

**HAZARDOUS COMBUSTION PRODUCTS:** Carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes, unidentified organic compounds.

**EXPLOSION HAZARDS:** Product as shipped is not a combustible dust. However, a combustible concentration of dust may occur when fines are suspended in air.

**FIRE FIGHTING PROCEDURES:** Standard procedures for Class A fires.

**FIRE FIGHTING EQUIPMENT:** As in any fire, wear self-contained pressure demand breathing apparatus, (MSHA/NIOSH approved or equivalent) and full protective gear.

**SENSITIVE TO STATIC DISCHARGE:** Static discharge could be an ignition source for a combustible concentration of dust.

**SENSITIVITY TO IMPACT:** Not Applicable

6. ACCIDENTAL RELEASE MEASURES

**SMALL SPILL:** Sweep up material and place in a disposal container.

**LARGE SPILL:** Vacuum or sweep up material and place in a disposal container.

**ENVIRONMENTAL PRECAUTIONS**

- **WATER SPILL:** Keep pellets out of waterways.
- **LAND SPILL:** Keep pellets out of storm sewers and ditches which lead to waterways.
- **AIR SPILL:** Not Applicable

**GENERAL PROCEDURES:** Vacuum or sweep up material and place in a disposal container.

**RELEASE NOTES:** None

**SPECIAL PROTECTIVE EQUIPMENT:** None

7. HANDLING AND STORAGE

**GENERAL PROCEDURES:** Keep away from heat, sparks and flame.

**HANDLING:** Ground and bond containers when transferring material.

**STORAGE:** This product may react with strong oxidizing agents and should not be stored near such materials. Store boxes and bags of material in areas protected with automatic sprinklers.

**STORAGE TEMPERATURE:** 60°C (140°F) maximum

**LOADING TEMPERATURE:** Not Determined

**STORAGE PRESSURE:** Not Determined
STORAGE TEMPERATURE: Store in a cool place below 140 F, 60 C.
LOADING TEMPERATURE NOTES: Not Determined
SHELF LIFE: Not Determined
SPECIAL SENSITIVITY: Not Determined
ELECTROSTATIC ACCUMULATION HAZARD: Material may accumulate static charges during transfers. Ground and bond containers when transferring material.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION
ENGINEERING CONTROLS: Provide adequate room ventilation. Provide adequate ventilation at the extruder to minimize exposure to process vapors. Eliminate ignition sources during repair and maintenance operations.

PERSONAL PROTECTIVE EQUIPMENT
EYES AND FACE: Wear safety glasses with side shields (or goggles).
SKIN: When handling or processing resins at elevated temperatures or in a molten state, wear protective clothing over the skin to prevent contact.
RESPIRATORY: A respiratory protection program that meets OSHA 1910.134, ANSI Z88.2 and/or CSA Z94.4-93 requirements must be followed whenever workplace conditions warrant use of a respirator.
PROTECTIVE CLOTHING: When handling or processing resins at elevated temperatures or in a molten state, wear protective clothing over the skin to prevent contact.
WORK HYGIENIC PRACTICES: Not Established
OTHER USE PRECAUTIONS: Eyewash fountains and safety showers should be easily accessible.

9. PHYSICAL AND CHEMICAL PROPERTIES
PHYSICAL STATE: Solid
ODOR: Slight hydrocarbon odor
APPEARANCE: Pellet
COLOR: Translucent to white
FREEZING POINT: Not Applicable
MELTING POINT: > 120°C (248°F)
DENSITY: Not Determined
SPECIFIC GRAVITY: 0.90 to 0.95
VIScosity: Not Available
MOLECULAR WEIGHT: Not Available

COMMENTS:
PHYSICAL STATE: None
VAPOR PRESSURE: Not Applicable
VAPOR DENSITY: Not Applicable
BOILING POINT: Not Applicable
WATER SOLUBILITY: Negligible
EVAPORATION RATE: Not Applicable

10. STABILITY AND REACTIVITY
STABLE: YES
HAZARDOUS POLYMERIZATION: NO

CONDITIONS TO AVOID: Keep away from heat, sparks and flame.

POLYMERIZATION: Product will not undergo polymerization.

HAZARDOUS DECOMPOSITION PRODUCTS: At elevated temperatures the material will begin to decompose, producing fumes that can contain carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes, unidentified organic compounds.

INCOMPATIBLE MATERIALS: Oxidizing materials.

11. TOXICOLOGICAL INFORMATION

GENERAL COMMENTS: Polybutylene Toxicological Information: In one study rats were fed a diet containing polybutylene powder at 1% and 10% in the diet for 6 months. No health effects were identified. There were no histopathology changes in body weight, clinical chemistry or on reproduction.

12. ECOLOGICAL INFORMATION

ENVIRONMENTAL DATA: Not Available

ECOTOXICOLOGICAL INFORMATION: Not Determined

DISTRIBUTION: Not Determined

CHEMICAL FATE INFORMATION: Not readily biodegradeable.

13. DISPOSAL CONSIDERATIONS

DISPOSAL METHOD: (1) Recycle (reprocess). (2) Incineration including energy recovery of waste material in a permitted facility in accordance with local, state or provincial and federal regulations. (3) Landfilling in a licensed facility in accordance with local, state or provincial and federal regulations.

RCRA HAZARD CLASS: This product is not judged to be a hazardous waste by any local, state or federal regulations; however, it may be listed as industrial waste in some states or provinces. This product is not listed in the U.S. federal hazardous waste regulations, 40 CFR 261.33 paragraphs (e) or (f), i.e., chemical products that are considered hazardous if they become wastes. It does not exhibit any of the hazardous characteristics listed in 40 CFR 261 Subpart C. State or local hazardous waste regulations may apply if different from the federal.

14. TRANSPORT INFORMATION

SPECIAL SHIPPING NOTES: This product is not regulated by DOT, IMO, IATA, Canadian TDG and associated regulations, ADR or RID.

15. REGULATORY INFORMATION

UNITED STATES

TSCA (TOXIC SUBSTANCE CONTROL ACT)

TSCA STATUS: All ingredients in this product are in compliance with TSCA.

OSHA HAZARD COMM. RULE: This product is not considered a hazardous material at temperatures below the melting point as determined by Basell according to OSHA definitions.

CLEAN WATER ACT: This product is regulated under EPA's Clean Water Act/NPDES rules as "floating material". In addition, this product is considered "significant material" under the EPA’s storm water permit rules.
CANADA

WHMIS (WORKER HAZARDOUS MATERIALS INFORMATION SYSTEM): This product is not considered a controlled substance under WHMIS. This MSDS meets WHMIS format requirements.

CANADIAN ENVIRONMENTAL PROTECTION ACT: All ingredients in this product are listed under CEPA on the DSL.

16. OTHER INFORMATION

APPROVED BY: Richard T. LeNoir   TITLE: Manager, Product Stewardship

REVISION SUMMARY New MSDS

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MATERIAL SAFETY DATA SHEET

Date-Issued: 07/16/2002
MSDS Ref. No: PB0400
Date-Revised: 07/17/2002
Revision No: New MSDS

Polybutene-1 PB 0400

1. PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Polybutene-1 PB 0400
PRODUCT DESCRIPTION: Polybutylene Homopolymer Pellets

MANUFACTURER
Basell USA Inc.
912 Appleton Road
Elkton, MD 21921-3920

Basell Canada Inc.
339 LaSalle Road
Corunna, Ontario
N0N 1G0
Product Stewardship: 410-996-1600

24 HR. EMERGENCY TELEPHONE NUMBERS
CHEMTREC (U.S.): (800) 424-9300
CANUTEC: (613) 996-6666

2. COMPOSITION / INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Wt.%</th>
<th>CAS#</th>
<th>EINECS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutylene</td>
<td>&gt;95</td>
<td>9003-28-5</td>
<td></td>
</tr>
<tr>
<td>Stabilizers (trade secret)</td>
<td>&lt;5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

COMMENTS: This product is not considered a hazardous material at temperatures below the melting point as determined by Basell according to the U.S. Occupational Safety and Health Act definitions and regulation, including the Hazard Communication Standard 29 CFR 1910.1200. This product is not considered a controlled substance by Basell according to Canada's WHMIS regulations. Threshold Limit Values (TLV) or Permissible Exposure Limit (PEL) values are not established. This material is not expected to cause physiologic impairment at low concentration. Until a specific TLV is adopted by ACGIH (American Conference of Governmental Hygienists), or an OSHA (Occupational Safety and Health Administration) PEL standard is issued, Basell suggests that this material be treated as a nuisance dust or particulate in accordance with the recommendations of ACGIH.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

PHYSICAL APPEARANCE: Translucent to white solid pellets

IMMEDIATE CONCERNS: Spilled material may present a slipping hazard. This product as shipped is not classified as a combustible dust; however, a combustible concentration of dust may occur if fines are suspended in air. Avoid contact with strong oxidizing agents. When working with the material at temperatures above the melting point, the material will begin to decompose producing fumes that can contain carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes and other unidentified organic compounds that come from the breakdown of the material. Adequate room and extruder ventilation should be provided to minimize exposures.
POTENTIAL HEALTH EFFECTS

EYES: Process vapors may irritate eyes.

SKIN: Exposure to molten resin may cause thermal burns.

INGESTION: Not Applicable

INHALATION: Process vapors may cause respiratory tract irritation.

SIGNS AND SYMPTOMS OF OVEREXPOSURE

EYES: Irritation or redness.

SKIN: Not Applicable

INGESTION: Not Applicable

INHALATION: Irritation of the nose, throat and respiratory tract.

ACUTE TOXICITY: Process vapors may cause eye and respiratory tract irritation.

CHRONIC: None Known

CARCINOGENICITY: None Known

MUTAGENICITY: None Known

REPRODUCTIVE TOXICITY

REPRODUCTIVE EFFECTS: None Known

TERATOGENIC EFFECTS: None Known

MEDICAL CONDITIONS AGGRAVATED: None Known

 ROUTES OF ENTRY: Eye, Inhalation

TARGET ORGAN STATEMENT: None Known

CANCER STATEMENT: This product is not considered to be a carcinogen by OSHA, IARC or NTP.

IRRITANCY: Exposure to process vapors may cause eye and respiratory tract irritation.

SENSITIZATION: None Known

WARNING CAUTION LABELS: Burn Risk - Avoid contact with molten resin. Explosion Risk - Prevent accumulation of dust particles. Slipping Risk - Keep walking surfaces free of spilled material. Vapor Risk - Provide ventilation to avoid exposure to process vapors.

COMMENTS HEALTH: None

HEALTH HAZARDS: Process vapors may cause eye and respiratory tract irritation.

PHYSICAL HAZARDS: Spilled material may present a slipping hazard. Exposure to molten resin may cause thermal burns.

4. FIRST AID MEASURES

EYES: Flush eyes with water for 15 minutes. Get medical attention.

SKIN: Molten Resin: If molten material comes in contact with the skin, cool under ice water or a running stream of water. DO NOT attempt to remove the material from the skin. Removal could result in severe tissue damage. Get medical attention.

INGESTION: Not Applicable

INHALATION: Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

ANTIDOTES: Not Applicable
5. FIRE FIGHTING MEASURES

**AUTOIGNITION TEMPERATURE:** Not Determined

**EXTINGUISHING MEDIA:** Use foam, carbon dioxide, or water spray when fighting fires involving this material.

**HAZARDOUS COMBUSTION PRODUCTS:** Carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes, unidentified organic compounds.

**EXPLOSION HAZARDS:** Product as shipped is not a combustible dust. However, a combustible concentration of dust may occur when fines are suspended in air.

**FIRE FIGHTING PROCEDURES:** Standard procedures for Class A fires.

**FIRE FIGHTING EQUIPMENT:** As in any fire, wear self-contained pressure demand breathing apparatus, (MSHA/NIST approved or equivalent) and full protective gear.

**SENSITIVE TO STATIC DISCHARGE:** Static discharge could be an ignition source for a combustible concentration of dust.

**SENSITIVITY TO IMPACT:** Not Applicable

6. ACCIDENTAL RELEASE MEASURES

**SMALL SPILL:** Sweep up material and place in a disposal container.

**LARGE SPILL:** Vacuum or sweep up material and place in a disposal container.

**ENVIRONMENTAL PRECAUTIONS**

**WATER SPILL:** Keep pellets out of waterways.

**LAND SPILL:** Keep pellets out of storm sewers and ditches which lead to waterways.

**AIR SPILL:** Not Applicable

**GENERAL PROCEDURES:** Vacuum or sweep up material and place in a disposal container.

**RELEASE NOTES:** None

**SPECIAL PROTECTIVE EQUIPMENT:** None

7. HANDLING AND STORAGE

**GENERAL PROCEDURES:** Keep away from heat, sparks and flame.

**HANDLING:** Ground and bond containers when transferring material.

**STORAGE:** This product may react with strong oxidizing agents and should not be stored near such materials. Store boxes and bags of material in areas protected with automatic sprinklers.

**STORAGE TEMPERATURE:** 60°C (140°F) maximum

**LOADING TEMPERATURE:** Not Determined

**STORAGE PRESSURE:** Not Determined
STORAGE TEMPERATURE: Store in a cool place below 140 F, 60 C.

LOADING TEMPERATURE NOTES: Not Determined

SHELF LIFE: Not Determined

SPECIAL SENSITIVITY: Not Determined

ELECTROSTATIC ACCUMULATION HAZARD: Material may accumulate static charges during transfers. Ground and bond containers when transferring material.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

ENGINEERING CONTROLS: Provide adequate room ventilation. Provide adequate ventilation at the extruder to minimize exposure to process vapors. Eliminate ignition sources during repair and maintenance operations.

PERSONAL PROTECTIVE EQUIPMENT

EYES AND FACE: Wear safety glasses with side shields (or goggles).

SKIN: When handling or processing resins at elevated temperatures or in a molten state, wear protective clothing over the skin to prevent contact.

RESPIRATORY: A respiratory protection program that meets OSHA 1910.134, ANSI Z88.2 and/or CSA Z94.4-93 requirements must be followed whenever workplace conditions warrant use of a respirator.

PROTECTIVE CLOTHING: When handling or processing resins at elevated temperatures or in a molten state, wear protective clothing over the skin to prevent contact.

WORK HYGIENIC PRACTICES: Not Established

OTHER USE PRECAUTIONS: Eyewash fountains and safety showers should be easily accessible.

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE: Solid

ODOR: Slight hydrocarbon odor

APPEARANCE: Pellet

COLOR: Translucent to white

FREEZING POINT: Not Applicable

MELTING POINT: > 120°C (248°F)

DENSITY: Not Determined

SPECIFIC GRAVITY: 0.90 to 0.95

VISCOSITY: Not Available

MOLECULAR WEIGHT: Not Available

COMMENTS:

PHYSICAL STATE: None

VAPOR PRESSURE: Not Applicable

VAPOR DENSITY: Not Applicable

BOILING POINT: Not Applicable

WATER SOLUBILITY: Negligible

EVAPORATION RATE: Not Applicable

10. STABILITY AND REACTIVITY

STABLE: YES
HAZARDOUS POLYMERIZATION: NO

CONDITIONS TO AVOID: Keep away from heat, sparks and flame.

POLYMERIZATION: Product will not undergo polymerization.

HAZARDOUS DECOMPOSITION PRODUCTS: At elevated temperatures the material will begin to decompose, producing fumes that can contain carbon dioxide, carbon monoxide, ketones, acrolein, aldehydes, unidentified organic compounds.

INCOMPATIBLE MATERIALS: Oxidizing materials.

11. TOXICOLOGICAL INFORMATION

GENERAL COMMENTS: Polybutylene Toxicological Information: In one study rats were fed a diet containing polybutylene powder at 1% and 10% in the diet for 6 months. No health effects were identified. There were no histopathology changes in body weight, clinical chemistry or on reproduction.

12. ECOLOGICAL INFORMATION

ENVIRONMENTAL DATA: Not Available

ECOTOXICOLOGICAL INFORMATION: Not Determined

DISTRIBUTION: Not Determined

CHEMICAL FATE INFORMATION: Not readily biodegradeable.

13. DISPOSAL CONSIDERATIONS

DISPOSAL METHOD: (1) Recycle (reprocess). (2) Incineration including energy recovery of waste material in a permitted facility in accordance with local, state or provincial and federal regulations. (3) Landfilling in a licensed facility in accordance with local, state or provincial and federal regulations.

RCRA HAZARD CLASS: This product is not judged to be a hazardous waste by any local, state or federal regulations; however, it may be listed as industrial waste in some states or provinces. This product is not listed in the U.S. federal hazardous waste regulations, 40 CFR 261.33 paragraphs (e) or (f), i.e., chemical products that are considered hazardous if they become wastes. It does not exhibit any of the hazardous characteristics listed in 40 CFR 261 Subpart C. State or local hazardous waste regulations may apply if different from the federal.

14. TRANSPORT INFORMATION

SPECIAL SHIPPING NOTES: This product is not regulated by DOT, IMO, IATA, Canadian TDG and associated regulations, ADR or RID.

15. REGULATORY INFORMATION

UNITED STATES

TSCA (TOXIC SUBSTANCE CONTROL ACT)

TSCA STATUS: All ingredients in this product are in compliance with TSCA.

OSHA HAZARD COMM. RULE: This product is not considered a hazardous material at temperatures below the melting point as determined by Basell according to OSHA definitions.

CLEAN WATER ACT: This product is regulated under EPA's Clean Water Act/NPDES rules as "floating material". In addition, this product is considered "significant material" under the EPA's storm water permit rules.
CANADA

WHMIS (WORKER HAZARDOUS MATERIALS INFORMATION SYSTEM): This product is not considered a controlled substance under WHMIS. This MSDS meets WHMIS format requirements.

CANADIAN ENVIRONMENTAL PROTECTION ACT: All ingredients in this product are listed under CEPA on the DSL.

16. OTHER INFORMATION

APPROVED BY: Richard T. LeNoir  TITLE: Manager, Product Stewardship

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APPENDIX C

NMR GRAPHS
Figure 1: 13C NMR spectrum of sample 59106_03 DP8010

C2(w%) = 4.5
Figure 2: 13C NMR spectrum of sample 59106_04 DP8310
C2(w%) = 5.0
Figure 3: 13C NMR spectrum of sample 58927_01 Br200
Figure 4: expanded region of 13C NMR spectrum of sample 58927_01 Br200 (CH2 branch)
Figure 5: 13C NMR spectrum of sample 58927_02 PB0110M
Figure 6: expanded region of 13C NMR spectrum of sample 58927_02 PB0110M (CH2 branches)
Figure 7: expanded region of 13C NMR spectrum of sample 58927_03 PB200
Figure 8: expanded region of $^{13}$C NMR spectrum of sample 58927_03 PB200 (CH$_2$ branches)
APPENDIX D

DSC CURVES
BR200
PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur = TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,15 mg

heat flow Q(W/g)

-1.5
-1
-0.5
0
0.5
1
1.5

temperature T(°C)

0 20 40 60 80 100 120 140 160 180 200

Tm-1 = 115,43 °C
dH-1 = 59,83 J/g
T-K = 76,80 °C
T-Krist.Max = 68,87 °C
Tm-2 = 112,35 °C
dH-2 = 44,50 J/g
DH-TK = 34,80 J/g
DSC-Apparatur = TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,91 mg

PB0110
PP&C Lab
Frankfurt
Dr. Gabriel

Tm-1 = 117,88 °C
dH-1 = 63,68 J/g
T-K = 87,56 °C
T-Krist.Max = 83,95 °C
Tm-2 = 114,27 °C
dH-2 = 45,60 J/g
DH-TK = 37,48 J/g
PB0200

PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur=TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,65 mg

Tm-1=114,21 °C
dH-1=52,68 J/g
T-K=64,42 °C
T-Krist.Max=51,90 °C
Tm-2=110,61 °C
dH-2=37,34 J/g
DH-TK=28,78 J/g
**PB0300**

PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur=TA Q1000
heating rate =10,00 K/min
cooling rate =10,00 K/min
sample mass =5,54 mg

<table>
<thead>
<tr>
<th>temperature T(°C)</th>
<th>heat flow Q(W/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm-1=113,38 °C</td>
<td>dH-1=51,63 J/g</td>
</tr>
<tr>
<td>T-K=68,18 °C</td>
<td>T-Krist.Max=57,96 °C</td>
</tr>
<tr>
<td>Tm-2=111,43 °C</td>
<td>dH-2=39,60 J/g</td>
</tr>
<tr>
<td>DH-TK=30,71 J/g</td>
<td></td>
</tr>
</tbody>
</table>

**1. heating run**

**2. heating run**

**cooling run**
1.heating run

cooling run

2.heating run

Tm-1=112,79 °C
dH-1=52,54 J/g
T-K=63,80 °C
T-Krist.Max=51,36 °C
Tm-2=110,68 °C
dH-2=37,57 J/g
DH-TK=28,16 J/g

DSC-Apparatur=TA Q1000
heating rate =10,00 K/min
cooling rate =10,00 K/min
sample mass =5,55 mg
$T_m-1=107.70 \, ^\circ C$
$\Delta H-1=55.87 \, J/g$
$T_K=65.27 \, ^\circ C$
$T_{Krist.\, Max}=56.76 \, ^\circ C$
$T_m-2=108.15 \, ^\circ C$
$\Delta H-2=38.56 \, J/g$
$\Delta H-TK=29.64 \, J/g$

DSC-Apparatur=TA Q1000
heating rate =10.00 K/min
cooling rate =10.00 K/min
sample mass =4.96 mg
DSC-Apparatur = TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,38 mg

PB0110M

PP&C Lab
Frankfurt
Dr. Gabriel

1. heating run
2. heating run

Tm-1 = 117,45 °C
dH-1 = 64,19 J/g
T-K = 79,93 °C
T-Kr. Max = 70,10 °C
Tm-2 = 115,35 °C
dH-2 = 44,66 J/g
DH-TK = 39,04 J/g
BR200
10 Day Storage

PP&C Lab
Frankfurt
Dr. Gabriel

Tm-1 = 123.37 °C
dH-1 = 62.61 J/g
T-K = 75.54 °C
T-Krist. Max = 66.94 °C
Tm-2 = 112.86 °C
dH-2 = 39.26 J/g
DH-TK = 31.00 J/g

DSC-Apparatur = TA Q1000
heating rate = 10.00 K/min
cooling rate = 10.00 K/min
sample mass = 5.15 mg
PB0110
10 Day Storage

PP&C Lab
Frankfurt
Dr. Gabriel

DSC Apparatur = TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,91 mg

Tm-1 = 127,09 °C
dH-1 = 67,23 J/g
T-K = 87,23 °C
T-Krist. Max = 83,60 °C
Tm-2 = 114,81 °C
dH-2 = 40,60 J/g
DH-TK = 34,66 J/g

heat flow Q(W/g)
temperature T(°C)
**PB0200**

10 Day Storage

PP&C Lab  
Frankfurt  
Dr. Gabriel

Temperature T(°C)

Heat flow Q(W/g)

- **1st heating run**
- **cooling run**
- **2nd heating run**

DSC-Apparatur=TA Q1000  
heating rate =10,00 K/min  
cooling rate =10,00 K/min  
sample mass =5,65 mg

- **T<sub>m</sub>-1=119,15 °C**  
- **dH-1=53,75 J/g**  
- **T-K=59,67 °C**  
- **T-Krist.Max=49,79 °C**  
- **Tm-2=111,12 °C**  
- **dH-2=32,31 J/g**  
- **DH-TK=26,25 J/g**
**PB0300 10 Day Storage**

**PP&C Lab**

**Frankfurt**

**Dr. Gabriel**

---

- **Tm-1** = 120.61 °C
- **dH-1** = 64.32 J/g
- **T-K** = 67.34 °C
- **T-Krist.Max** = 57.05 °C
- **Tm-2** = 111.68 °C
- **dH-2** = 38.39 J/g
- **DH-TK** = 29.39 J/g

---

**DSC-Apparatur** = TA Q1000

- **heating rate** = 10.00 K/min
- **cooling rate** = 10.00 K/min
- **sample mass** = 5.54 mg

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**22-02-07**
PB0400
10 Day Storage

PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur=TA Q1000
heating rate =10,00 K/min
cooling rate =10,00 K/min
sample mass =5,55 mg

Tm-1=117,97 °C
dH-1=64,98 J/g
T-K=64,70 °C
T-Krist.Max=48,00 °C
Tm-2=110,86 °C
dH-2=36,15 J/g
DH-TK=26,32 J/g

Temperature T(°C)
Heat flow Q(W/g)
PB0800
10 Day Storage

PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur=TA Q1000
heating rate =10,00 K/min
cooling rate =10,00 K/min
sample mass =4,96 mg

Tm-1=116,85 °C
dH-1=67,37 J/g
T-K=63,42 °C
T-Krist.Max=56,29 °C
Tm-2=108,27 °C
dH-2=35,68 J/g
DH-TK=27,67 J/g
PB0110M
10 Day Storage

PP&C Lab
Frankfurt
Dr. Gabriel

DSC Apparatur = TA Q1000
heating rate = 10,00 K/min
cooling rate = 10,00 K/min
sample mass = 5,38 mg

1. heating run
2. heating run

- $T_{m-1} = 123.98 \, ^\circ C$
- $dH_{-1} = 68.76 \, J/g$
- $T_{K} = 79.77 \, ^\circ C$
- $T_{Krist. Max} = 69.31 \, ^\circ C$
- $T_{m-2} = 115.62 \, ^\circ C$
- $dH_{-2} = 42.59 \, J/g$
- $D_{H-TK} = 37.02 \, J/g$

$T$ vs $Q$ graph:
- 0 to 200 °C
- 0 to 2.00 W/g

1. heating run
2. cooling run
1. heating run

22-02-07
**Heat flow Q (W/g)**

- **1. heating run**
  - $T_m - 1 = -1.00 \, ^\circ C$
  - $dH - 1 = -1.00 \, J/g$
  - $T - K = -1.00 \, ^\circ C$
  - $T - Krist. Max = -1.00 \, ^\circ C$
  - $T_m - 2 = -1.00 \, ^\circ C$
  - $dH - 2 = -1.00 \, J/g$
  - $DH - TK = -1.00 \, J/g$

- **2. heating run**

**DSC Apparatur = TA**

- $Q_{1000}$ heating rate = 10.00 K/min
- cooling rate = 10.00 K/min
- sample mass = 5.35 mg
DSC-Apparatur=TA Q1000
heating rate =10.00 K/min
cooling rate =10.00 K/min
sample mass =5.38 mg

DSC Diagram:
- Heating run (solid black line)
- Cooling run (dotted red line)

Temperature T (°C):
- Tm-1=-1.00 °C
- T-K=-1.00 °C
- T-Krist.Max=-1.00 °C
- Tm-2=-1.00 °C
- DH-TK=-1.00 J/g

Heat flow Q (W/g):
- dH-1=-1.00 J/g
- dH-2=-1.00 J/g
BR200-X1
PP&C Lab
Frankfurt
Dr.Gabriel

DSC-Apparatur=TA Q1000
heating rate =10.00 K/min
cooling rate =10.00 K/min
sample mass =5.89 mg

1. heating run
2. heating run
cooling run

T_m-1=118.46 °C
d_H-1=50.29 J/g
T_K=80.14 °C
T_Krist. Max=74.78 °C
T_m-2=112.59 °C
d_H-2=31.65 J/g
D_H-T_K=31.18 J/g
BR200-X2
PP&C Lab
Frankfurt
Dr. Gabriel

DSC-Apparatur=TA Q1000
heating rate =10.00 K/min
cooling rate =10.00 K/min
sample mass =5.48 mg

Tm-1=117.63 °C
dH-1=55.16 J/g
T-K=91.23 °C
T-Krist.Max=88.08 °C
Tm-2=114.16 °C
dH-2=37.21 J/g
DH-TK=37.04 J/g

1.heating run
cooling run
2.heating run
JOURNAL PUBLICATIONS


CONFERENCE PROCEEDINGS


248