

# High-Pressure Crystallization of Poly(1-butene)

Bc. Jiří Kalous

---

Master Thesis  
2010

 Tomas Bata University in Zlín  
Faculty of Technology

---

Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů

akademický rok: 2009/2010

## ZADÁNÍ DIPLOMOVÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Bc. Jiří KALOUS**

Studijní program: **N 2808 Chemie a technologie materiálů**

Studijní obor: **Inženýrství polymerů**

Téma práce: **Vysokotlaká krystalizace poly(1-butenu)**

Zásady pro vypracování:

**Vypracujte literární rešerši na dané téma (aspekty vysokotlaké krystalizace).**

**Provedte vysokotlakou krystalizaci a tání isotaktických poly(1-butenů).**

**Vzorky zhodnoťte pomocí vhodných experimentálních metod a diskutujte dosažené výsledky.**

Rozsah práce:

Rozsah příloh:

Forma zpracování diplomové práce: **tištěná/elektronická**

Seznam odborné literatury:

LUYE, J.-F. -- REGNIER, G. -- BOT, P. -- DELAUNAY, D. -- FULCHIRON, R.: PVT Measurement Methodology for Semicrystalline Polymers to Simulate Injection-Molding Process. *J. Appl. Polym. Sci.*, 2001, vol. 79, pp. 302-311.

OBADAL, M. -- ČERMÁK, R. -- STOKLASA, K.; Tailor-made 3-phase crystalline systems in isotactic polypropylene, *Macromol. Rapid Comm.*, submitted 2005

SPERLING, L. H.: *Introduction to Physical Polymer Science*. 3rd. edition, Wiley-Interscience, 2001. 671 p. ISBN 0-471-32921-5

MARING D., et al. *J. Polym. Sci.* 2000, Vol. 38, p. 2611.

Vedoucí diplomové práce: **Ing. Lubomír Beníček, Ph.D.**  
Ústav inženýrství polymerů

Datum zadání diplomové práce: **15. února 2010**

Termín odevzdání diplomové práce: **14. května 2010**

Ve Zlíně dne 15. února 2010



doc. Ing. Petr Hlaváček, CSc.  
*děkan*



doc. Ing. Roman Čermák, Ph.D.  
*ředitel ústavu*

## PROHLÁŠENÍ

Prohlašuji, že

- beru na vědomí, že odevzdáním diplomové/bakalářské práce souhlasím se zveřejněním své práce podle zákona č. 111/1998 Sb. o vysokých školách a o změně a doplnění dalších zákonů (zákon o vysokých školách), ve znění pozdějších právních předpisů, bez ohledu na výsledek obhajoby <sup>1)</sup>;
- beru na vědomí, že diplomová/bakalářská práce bude uložena v elektronické podobě v univerzitním informačním systému dostupná k nahlédnutí, že jeden výtisk diplomové/bakalářské práce bude uložen na příslušném ústavu Fakulty technologické UTB ve Zlíně a jeden výtisk bude uložen u vedoucího práce;
- byl/a jsem seznámen/a s tím, že na moji diplomovou/bakalářskou práci se plně vztahuje zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, zejm. § 35 odst. 3 <sup>2)</sup>;
- beru na vědomí, že podle § 60 <sup>3)</sup> odst. 1 autorského zákona má UTB ve Zlíně právo na uzavření licenční smlouvy o užití školního díla v rozsahu § 12 odst. 4 autorského zákona;
- beru na vědomí, že podle § 60 <sup>3)</sup> odst. 2 a 3 mohu užít své dílo – diplomovou/bakalářskou práci nebo poskytnout licenci k jejímu využití jen s předchozím písemným souhlasem Univerzity Tomáše Bati ve Zlíně, která je oprávněna v takovém případě ode mne požadovat přiměřený příspěvek na úhradu nákladů, které byly Univerzitou Tomáše Bati ve Zlíně na vytvoření díla vynaloženy (až do jejich skutečné výše);
- beru na vědomí, že pokud bylo k vypracování diplomové/bakalářské práce využito softwaru poskytnutého Univerzitou Tomáše Bati ve Zlíně nebo jinými subjekty pouze ke studijním a výzkumným účelům (tedy pouze k nekomerčnímu využití), nelze výsledky diplomové/bakalářské práce využít ke komerčním účelům;
- beru na vědomí, že pokud je výstupem diplomové/bakalářské práce jakýkoliv softwarový produkt, považují se za součást práce rovněž i zdrojové kódy, popř. soubory, ze kterých se projekt skládá. Neodevzdání této součásti může být důvodem k neobhájení práce.

Ve Zlíně: 17.5.2010

.....

---

<sup>1)</sup> zákon č. 111/1998 Sb. o vysokých školách a o změně a doplnění dalších zákonů (zákon o vysokých školách), ve znění pozdějších právních předpisů, § 47 Zveřejňování závěrečných prací:

(1) Vysoká škola nevydělečně zveřejňuje disertační, diplomové, bakalářské a rigorózní práce, u kterých proběhla obhajoba, včetně posudků oponentů a výsledku obhajoby prostřednictvím databáze kvalifikačních prací, kterou spravuje. Způsob zveřejnění stanoví vnitřní předpis vysoké školy.

(2) Disertační, diplomové, bakalářské a rigorózní práce odevzdané uchazečem k obhajobě musí být též nejméně pět pracovních dnů před konáním obhajoby zveřejněny k nahlížení veřejnosti v místě určeném vnitřním předpisem vysoké školy nebo není-li tak určeno, v místě pracoviště vysoké školy, kde se má konat obhajoba práce. Každý si může ze zveřejněné práce pořizovat na své náklady výpisy, opisy nebo rozmnoženiny.

(3) Platí, že odevzdáním práce autor souhlasí se zveřejněním své práce podle tohoto zákona, bez ohledu na výsledek obhajoby.

<sup>2)</sup> zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, § 35 odst. 3:

(3) Do práva autorského také nezasahuje škola nebo školské či vzdělávací zařízení, užije-li nikoli za účelem přímého nebo nepřímého hospodářského nebo obchodního prospěchu k výuce nebo k vlastní potřebě dílo vytvořené žákem nebo studentem ke splnění školních nebo studijních povinností vyplývajících z jeho právního vztahu ke škole nebo školskému či vzdělávacímu zařízení (školní dílo).

<sup>3)</sup> zákon č. 121/2000 Sb. o právu autorském, o právech souvisejících s právem autorským a o změně některých zákonů (autorský zákon) ve znění pozdějších právních předpisů, § 60 Školní dílo:

(1) Škola nebo školské či vzdělávací zařízení mají za obvyklých podmínek právo na uzavření licenční smlouvy o užití školního díla (§ 35 odst. 3). Odpírá-li autor takového díla udělit svolení bez vážného důvodu, mohou se tyto osoby domáhat nahrazení chybějícího projevu jeho vůle u soudu. Ustanovení § 35 odst. 3 zůstává nedotčeno.

(2) Není-li sjednáno jinak, může autor školního díla své dílo užit či poskytnout jinému licenci, není-li to v rozporu s oprávněnými zájmy školy nebo školského či vzdělávacího zařízení.

(3) Škola nebo školské či vzdělávací zařízení jsou oprávněny požadovat, aby jim autor školního díla z výdělku jím dosaženého v souvislosti s užitím díla či poskytnutím licence podle odstavce 2 přiměřeně přispěl na úhradu nákladů, které na vytvoření díla vynaložily, a to podle okolností až do jejich skutečné výše; přitom se přihlédne k výši výdělku dosaženého školou nebo školským či vzdělávacím zařízením z užití školního díla podle odstavce 1.

## **ABSTRACT**

This work investigates high pressure behavior of two different, commercially available poly(1-butens). Each of the material was subduced to non-isothermal crystallization and melting at pressure range from 20 to 200 MPa at pVT 100 device. After this measurement, specific pressures were chosen from previous range and samples were prepared at these chosen pressures to investigate influence of non-isothermal crystallization and melting at increased pressures. After preparation, samples were investigated by using wide-angle X-Ray scattering, differential scanning calorimetry, density measurement and polarized light microscopy to reveal polymorphic structure, melting of the sample and its morphology. Results showed influence of two homopolymers of poly(1-butene) at high-pressure behavior and also influence of pressures on formation of metastable phase I' and II.

Key words: poly(1-butene), high-pressure crystallization, morphology, thermal behavior

## **ABSTRAKT**

Tato práce se zabývá vysokotlakým chování dvou rozdílných, komerčně dostupných, poly(1-butenů). Každý z materiálů byl nejprve podroben neizotermní krystalizaci a tání v rozsahu tlaků 20 až 200MPa na zařízení pVT 100. Poté byly z této řady vybrány specifické tlaky, pro které byly připraveny samostatné vzorky, za účelem podrobnějšího zkoumání vlivu neizotermní krystalizace a tání při zvýšených tlacích. Takto připravené vzorky byly zkoumány pomocí metody širokoúhlové rentgenografie, diferenciální snímací kalorimetrie, měření hustoty a optické mikroskopie pro zjištění polymorfni struktury, tání vzorku a jeho morfologie. Výsledky ukázaly vliv dvou homopolymerů poly(1-butenů) na vysokotlaké chování a také vliv tlaků na tvorbu metastabilních forem I' a II

Klíčová slova: poly(1-buten), vysokotlaká krystalizace, morfologie, tepelné chování

## Acknowledgement

I would like to thank to my supervisor, Ing. Lubomír Beníček PhD., for his advices, valuable time, help during the measurement and overall support during work on my Master thesis.

I declare that I worked on this Master thesis by myself, I have mentioned all used literature and the delivered Master thesis is exactly the same as the Master thesis uploaded to IS/STAG.

Zlín, 17.5. 2010

---

Jiří Kalous

# CONTENT

<b>INTRODUCTION .....</b>	<b>10</b>
<b>I THEORETICAL BACKGROUND.....</b>	<b>11</b>
<b>1 POLY(1-BUTENE) .....</b>	<b>12</b>
1.1 PROPERTIES OF POLY(1-BUTENE) .....	12
1.2 PREPARATION OF POLY-1-BUTENE .....	12
1.3 CRYSTAL MODIFICATIONS.....	13
1.3.1 Crystal phase I and I' .....	13
1.3.2 Crystal phase II.....	15
1.3.3 Crystal phase III.....	15
1.4 PHASE TRANSFORMATION.....	16
1.4.1 X-Ray diffraction investigation of the phase transformation.....	17
1.4.2 Electron diffraction investigation of phase transformation.....	19
1.4.3 Microindentation hardness investigation of phase transformation.....	20
1.4.4 AFM investigation of phase transformation.....	20
<b>2 KINETICS OF ISOTHERMAL AND NON-ISOTHERMAL CRYSTALIZATION.....</b>	<b>21</b>
2.1 COMMON MODELS OF ISOTHERMAL CRYSTALIZATION.....	21
2.1.1 The Avrami Equation .....	21
2.1.2 Keith-Padden Kinetics of Spherulic crystallization .....	22
2.1.3 Hoffman's nucleation theory.....	23
2.2 MODELS OF NON-ISOTHERMAL CRYSTALLIZATION.....	24
2.2.1 Ziabicki's equation .....	24
2.2.2 Nakamura's equation.....	25
2.2.3 Ozawa's equation .....	26
2.2.4 Experimental observation on isotactic poly-1-butene .....	26
<b>3 USED METHODS OF ANALYSIS .....</b>	<b>27</b>
3.1 POLARIZED LIGHT MICROSCOPY.....	27
3.2 DIFFERENTIAL SCANNING CALORIMETRY .....	28
3.3 X-RAY DIFFRACTION .....	29
3.4 DENSITY MEASUREMENT .....	29
<b>II EXPERIMENTAL .....</b>	<b>31</b>
<b>4 SAMPLE PREPARATION .....</b>	<b>32</b>
4.1 PVT DEVICE SAMPLE PREPARATION .....	32
4.2 POLARIZED LIGHT MICROSCOPY SPECIMEN PREPARATION.....	35
4.3 DSC SPECIMEN PREPARATION .....	35
4.4 WAXS SPECIMEN PREPARATION .....	36
<b>III RESULTS AND DISCUSSION.....</b>	<b>37</b>



<b>5</b>	<b>DSC RESULTS.....</b>	<b>38</b>
5.1	DP 0401M DSC CURVES DISCUSSION .....	40
5.2	PB 0300M DSC CURVES DISCUSSION .....	41
5.3	SAMPLE COMPARISON.....	42
<b>6</b>	<b>X-RAY DIFFRACTION RESULTS.....</b>	<b>43</b>
6.1	X-RAY DIFFRACTION RESULTS DISCUSSION .....	45
<b>7</b>	<b>DENSITY MEASUREMENT RESULTS.....</b>	<b>46</b>
7.1	DENSITY MEASUREMENT RESULTS DISCUSSION .....	47
<b>8</b>	<b>PVT SAMPLE MEASUREMENT RESULTS .....</b>	<b>48</b>
8.1	DP 0401M CRYSTALLIZATION AND MELTING TEMPERATURES .....	48
8.2	PB 0300M CRYSTALLIZATION AND MELTING TEMPERATURES .....	50
8.3	TEMPERATURES ANOMALIES DISCUSSION .....	52
<b>9</b>	<b>POLARIZED LIGHT MICROSCOPY RESULTS .....</b>	<b>53</b>
	<b>CONCLUSION .....</b>	<b>58</b>
	<b>REFERENCES.....</b>	<b>60</b>
	<b>LIST OF SYMBOLS AND ABBREVIATIONS .....</b>	<b>63</b>
	<b>LIST OF FIGURES .....</b>	<b>65</b>
	<b>LIST OF TABLES.....</b>	<b>67</b>

## INTRODUCTION

Polymers are able to replace lots of traditional materials, often with a better result, and they are widely used materials in many branches of the industry. Most demanded properties are low cost and high mechanical and chemical properties of the material. This leads to high level of competition between different polymers and even between modifications of the same polymer. Poly(1-butene) is almost as old as polypropylene but its usage is not so wide-spread. However, in last few years its number of applications is increasing, especially in pipes for hot water and applications where high creep resistance or abrasive resistance is required.

When poly(1-butene) is crystallized on atmospheric pressure from melt, it crystallize in phase II, which is metastable and during few days it recrystallizes into stable phase I. This is combined with high shrinkage and increase of the mechanical properties. When poly(1-butene) is prepared under high pressure, it crystallize in phase I'. Different pressure of crystallization means a different shrinkage after period of time. Mechanism of the phase transformation is not yet fully discovered and its revelation could be a great help in practical use of poly(1-butene). There are many factors influencing crystallization, like molecular weight, heat conduction and pressure of crystallization and combination of these factors.

Main goal of this work is to inspect high-pressure, non-isothermal crystallization and melting of the isotactic poly(1-butene) samples and to find how these conditions influence morphology, phase composition and density of the sample. To reveal acquired structure and phase composition after samples crystallization at different pressures at pVT 100 device, morphology was studied by polarized light microscopy, phase composition was revealed by differential scanning calorimetry (DSC) and wide-angle X-Ray scattering (WAXS) and density was measured by using laboratory scales.

## **I. THEORETICAL BACKGROUND**

## 1 POLY(1-BUTENE)

Poly(1-butene) belongs to the group of polyolefins. First poly-1-butene was produced by Nestolen BT by Chemische Werke Hüls in Germany, named Vestolen BT. It has been used for water pipes since mid 1960's. Nowadays it is produced by LyondellBasell company. However, poly(1-butene) is still not fully explored polymer. It has many properties similar to other polyolefins but also some uncommon properties. [1]

### 1.1 Properties of Poly(1-butene)

Poly(1-butene) (PB-1) is thermoplastic polyolefin with very good mechanical properties, like a low stiffness, good elastic recovery, and very high abrasive resistance, which is comparable to ultra-high molecular weight polyethylene in wet conditions. Also its creep resistance is very high. It possesses common properties like other polyolefins, i.e. chemical resistance, electrical insulation etc. Resistance to aliphatic hydrocarbons is lower than polyethylene and polypropylene but resistance to environmental stress cracking is excellent. When compared to lighter polyolefins (PE,PP), it is more expensive and its properties are influenced by crystal structure transformation.[2] Common density is around 0,9 g/cm<sup>3</sup>, but this may vary due to phase change (aging). Its molecular weight lies between 770 000 and 3 300 000. When crystallized from melt, crystallinity is 30-35% but after phase change crystallinity increases to 50-55%. [3]

### 1.2 Preparation of Poly-1-butene

Poly(1-butene) is prepared by stereospecific Ziegler – Natta catalyst polymerization of butene-1 in solvent. This results in linear, isotactic, high molecular weight and semi-crystalline polymer. Also metallocene catalysts can be used. During polymerization, catalyst dissociates and atactic part of the polymer is removed.[4]

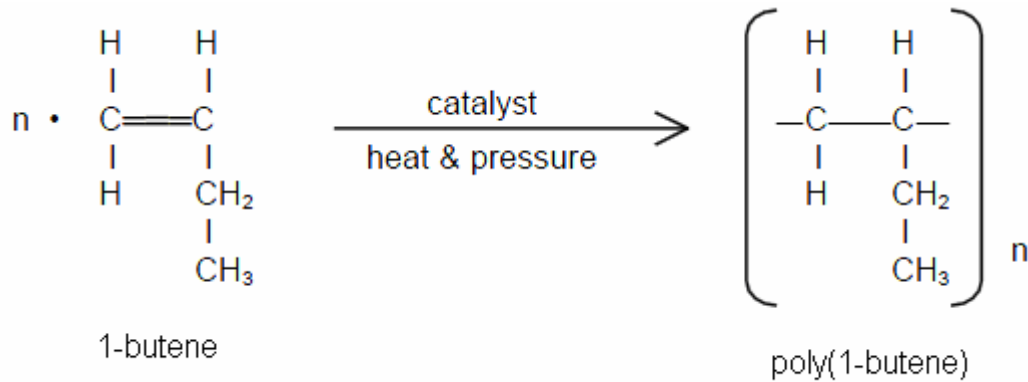


Fig. (1) Scheme of poly(1-butene) polymerization[4]

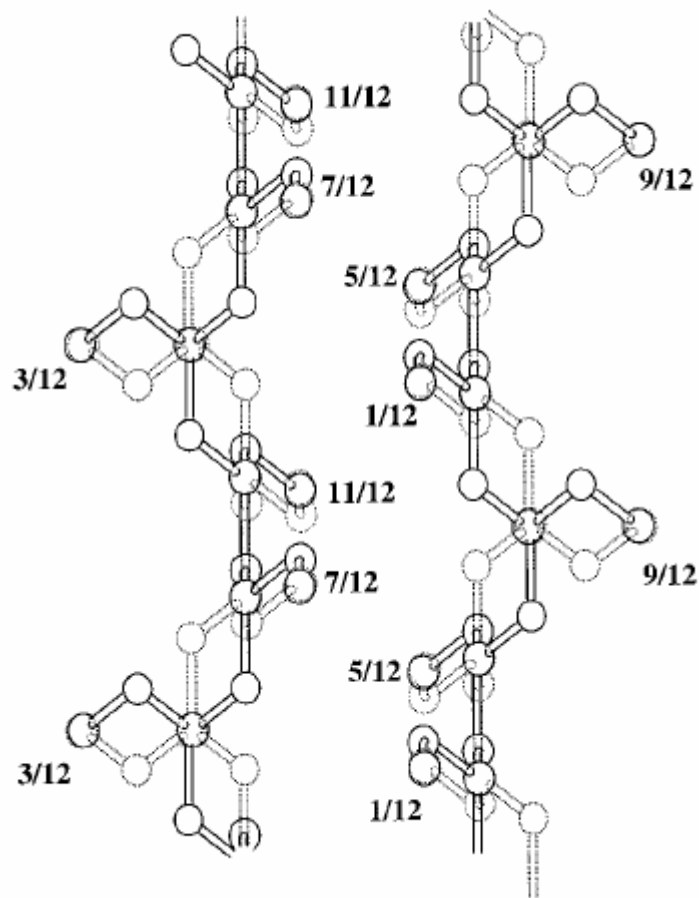
### 1.3 Crystal modifications

Polymorphic behavior is very complex, because it can crystallize in various crystalline forms. There are three different phases, which are further divided into modifications, marked as '. By using X-Ray diffraction phase I and I' cannot be distinguished

#### 1.3.1 Crystal phase I and I'

Crystal phase I have 3/1 twinned helix conformation and hexagonal unit cell ( $a = 17,7 \text{ \AA}$  and  $c = 6,5 \text{ \AA}$ ).[5] Phase I is product of phase transformation of phase II.

When the melt crystallization is executed under high pressure, phase I' appears, which has untwined 3/1 helix. Melting temperatures are different for each phase. Phase I melts at  $130 \text{ }^\circ\text{C}$  and phase I' melts at  $90\text{-}95 \text{ }^\circ\text{C}$  even though they show the same crystal structure. Phase I have heat of fusion  $141 \text{ J/g}$ . [6]. Crystal phase I is shown at fig. (2)



*Fig. (2) 3/1 helix packing in form I [5]*

However, under specific conditions, phase I can crystallize directly from melt under atmospheric pressure, which is very important for industry. S. Acernion et al. [7] prepared poly(1-butene) with phase I directly from the melt by employing build-in stereodeflects (rr triads defects) and regiodeflects(4,1 units). Poly-1-butenes with these defects were prepared by using  $C_1$  and  $C_2$ -symmetric metallocene catalyst. Concentration of the defects was driven by choice of ligand structure of the regiospecific  $C_1$ -symmetric catalyst. Highly isotactic samples with concentration of rr stereodeflects lower than 2 mol% crystallize to form II. Stereodeflective samples with concentration of rr stereodeflects crystallize to form I directly from melt. This is shown at figure (3).

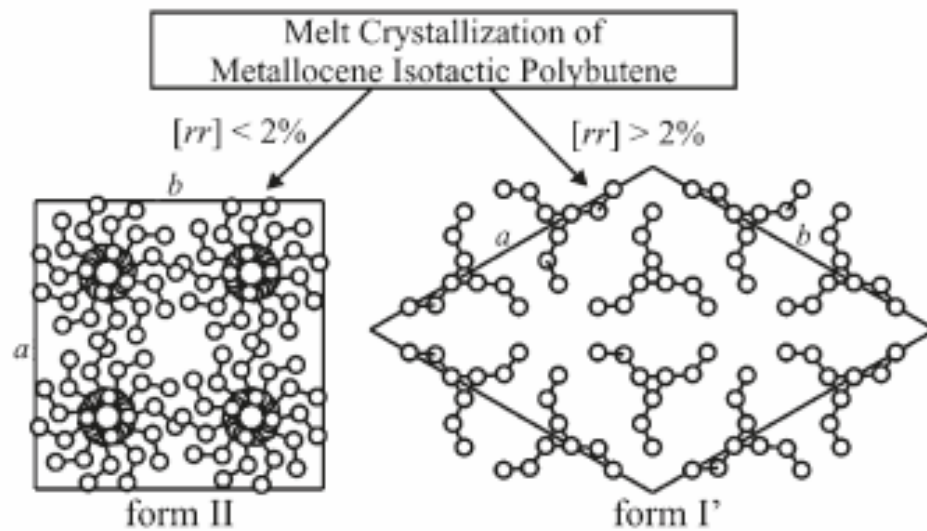


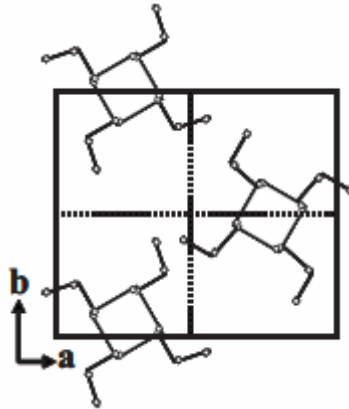
Fig. (3) Scheme of polymorphic behavior of metallocene made poly-1-butene [7]

### 1.3.2 Crystal phase II

Melt crystallization under atmospheric pressure leads to form II, which is tetragonal form with 11/3 helix conformation. Phase II possesses a tetragonal unit cell ( $a = 15 \text{ \AA}$  and  $c = 20.9 \text{ \AA}$ ). (23) This modification is metastable and changes to form I during few days. Phase II has a heat of fusion of  $62 \text{ J/g}$  [6]. The melt temperature of phase II is  $124 \text{ }^\circ\text{C}$  [7].

### 1.3.3 Crystal phase III

During the crystallization from solution, PB-1 will crystallize in orthorhombic form with 4/1 helix, marked as phase III. [2] It can also be crystallized from melt under high pressure and with the addition of specific nucleating agents. [7] Form III is the least stable of all three forms above  $95 \text{ }^\circ\text{C}$  and quickly transforms to form II, which then slowly transforms to form I. Under  $95 \text{ }^\circ\text{C}$ , it is relatively stable [8]. Phase III is shown in fig. (4).



*Fig. (4) Unit cell of form III in isotactic poly-1-butene [9]*

#### 1.4 Phase transformation

The spontaneous crystal to crystal transformation from phase II to phase I was discovered by Natta et al. in their early works. This transformation was investigated in details, because it is similar to solid-state crystal transformation in other polymers and considerably limits practical applications of poly(1-butene). [10] The mechanism of II to I transformation is not yet fully understood. It is known that transformation occurs via nucleation in crystal sites that are locally under stress. During the transformation, crystallinity does not change. Crystal morphology does not alternate either. [11] Speed of this transformation is maximal at room temperature and it is accelerated by applying stress deformation. Effects of this transformation are shrinkage, increase of stiffness, hardness and tensile strength. [12]



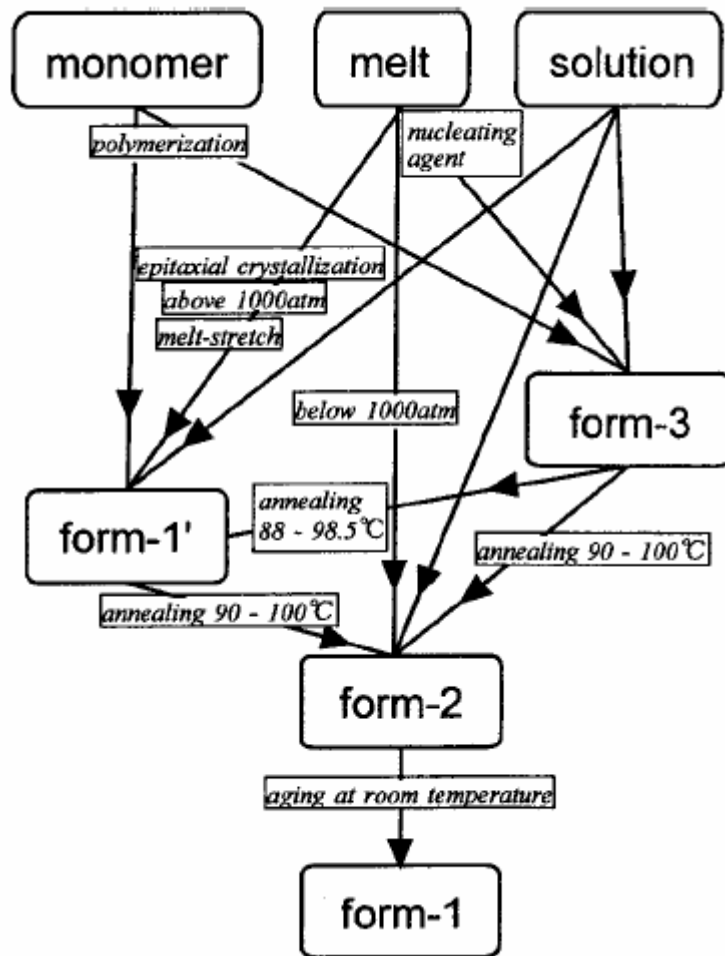
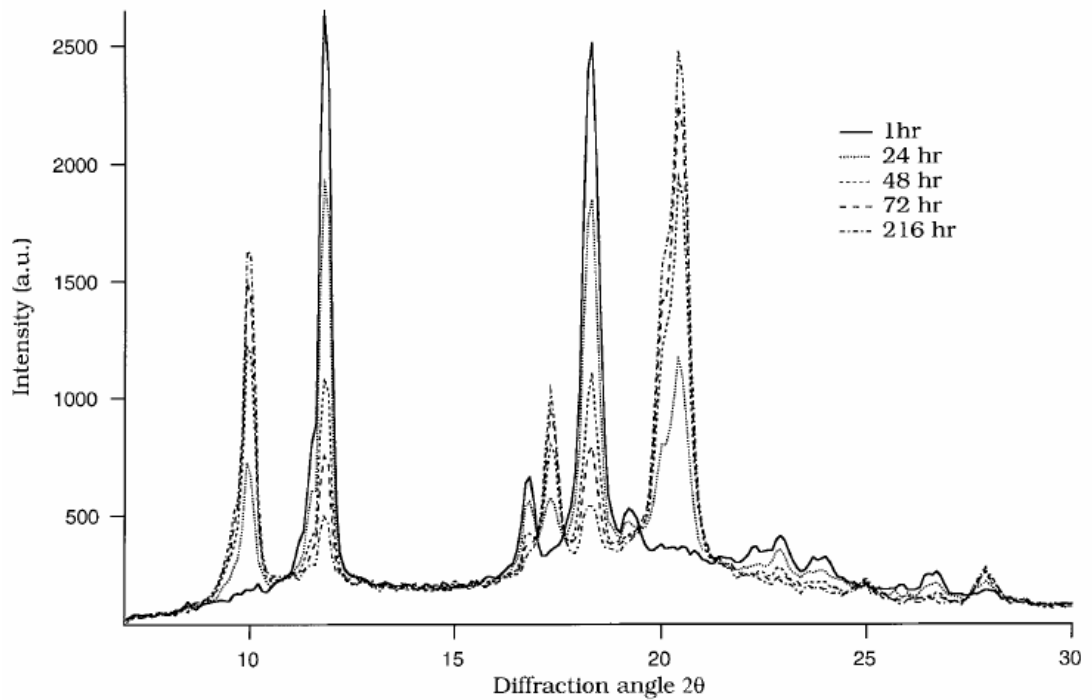


Fig. (5) Scheme of crystallization and phase transformation of poly-1-butene [13]

#### 1.4.1 X-Ray diffraction investigation of the phase transformation

One of the methods to describe II to I transformation is using X-Ray (WAXS,SAXS). From WAXS and SAXS results, Antonio M. [14] concluded, that a twofold mechanism takes a place during II to I transformation. The transition nucleation seems to be localized on lamer distortion points and the transition itself involves the rearrangement of lamellae and lamellar stacks. Further crystallization of amorphous phase to phase I also occurs, creating new thin lamellae inside lamellar stacks [14]. This is in conflict with statement of C. D. Rossa and co. [7], who says that crystallinity does not change during phase transformation.



*Fig. (6) Phase II to I transformation captured by WAXS [14]*

The phase transformation does not affect the surface morphology in either melt-crystallized samples or solution growth crystals. In melt-crystallized material, nucleation occurs at random places in a spherulite. From one the one tetragonal crystal (phase II), multiple twinned hexagonal (phase I) crystals arise. Multiple nucleation occur in a single tetragonal lamella. Also, second, slower stage of nucleation is observed in poly(1-butene). [15]

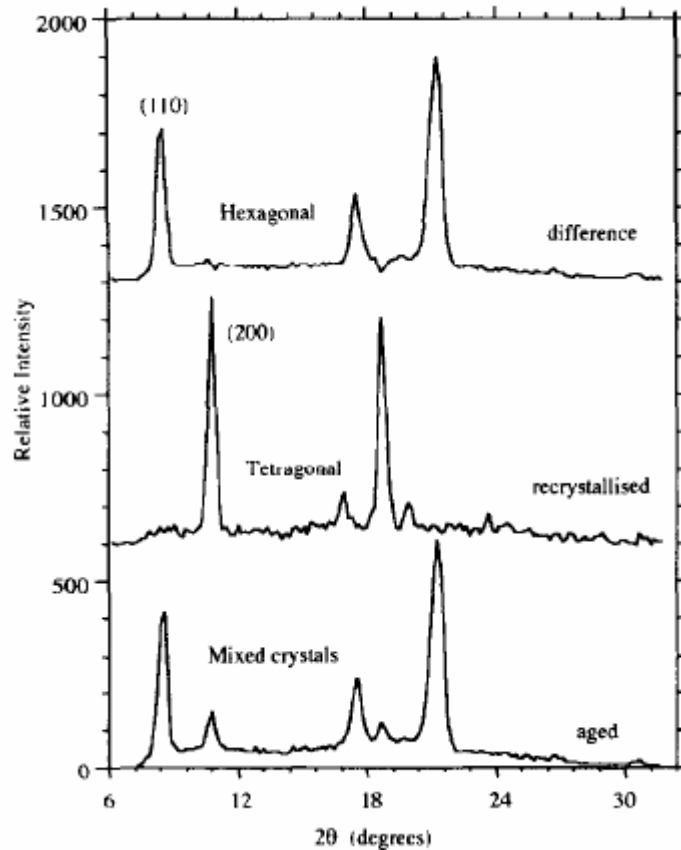


Fig. (7) Characteristics WAXS patterns for hexagonal and tetragonal forms [16]

#### 1.4.2 Electron diffraction investigation of phase transformation

Whole single crystals were observed by S. Kopp et al. [10] by using electron diffraction and bright- and dark-field imaging of solution and thin-film grown single crystals. In many crystals, double twinned phase I after transformation is observed but the vast majority of transformed monolamellar crystals display single phase I orientation. Dark-field imaging confirms that boundaries between twinned phase I and single phase I domains do not follow growth sector boundaries. However, exact nature of the mechanism which initiate the transition is not yet known. [10]

### 1.4.3 Microindentation hardness investigation of phase transformation

Microindentation hardness is method, which can easily distinguish between phase II and phase I of poly(1-butene). As F. Azzuri et al. [17] measured, microindentation hardness of phase I significantly higher than phase II. Reason is higher chain packing in phase I. By using this method, good agreement with melting enthalpy measurement was found. Results shows, that the rate of phase transformation does not depend on the molecular mass of the poly(1-butene) samples measured. However, hardness of the each phase is influenced by molecular weight of the poly(1-butene).[18] Also, speed of the transformation is influenced by the rate of cooling during sample preparation. When sample is cooled rapidly, transformation takes around 12 day. For samples isothermally crystallized, transformation it takes 7 days.

### 1.4.4 AFM investigation of phase transformation

Poly(1-butene) in melt-crystallized ultra-thin film at different temperatures were studied by AFM in tapping mode by Shidong J. et al. Spherulites with closely packed edge-on lamellae and lathlike flat-on crystals were observed and melting processes after different periods of time were monitored. By using the method of selective melting, less stable phase II was removed and form II to form I transformation was observed. It was found that nucleation of phase I crystals is the rate-determining factor of the transformation. Combining the facts that nucleation of the stable Form I crystals starts most likely at crystalline side surfaces or corners, and the phase conversion rate of the melt grown flat-on crystals is much faster than that of the solution grown single crystals leads to a theory that residual local thermal stresses exist at the edges of the microcrystallites and stacking regularity of the crystalline lamellae play a very important role in generating the nuclei of the form I crystals. [19]

## 2 KINETICS OF ISOTHERMAL AND NON-ISOTHERMAL CRYSTALLIZATION

A lot of traditional studies of crystallization are limited to constant and idealized conditions (pressure, temperature, etc.). However, in real situations, conditions may be changing over time. It leads to state, when crystallization is dependant on actual conditions as well as on the speed of change of conditions. Crystallization is ruled by the laws of thermodynamics, which defines if the crystal can or cannot exist under current conditions. Speed of crystallization is defined by kinetics of the process. [20]

### 2.1 Common models of isothermal crystallization

#### 2.1.1 The Avrami Equation

To describe crystallization under isothermal conditions, Avrami equation is used. It allows us to calculate crystallinity fraction as a function of elapsed time. General form of Avrami equation is:

$$1 - X_{(t)} = \exp(-Kt^n) \quad (1)$$

Which is also used in logarithmic form

$$\ln(1 - X_{(t)}) = -Kt^n \quad (2)$$

Where  $X_{(t)}$  is the crystallinity fraction in the crystallizable material at time  $t$ .  $K$  and  $n$  are constants typical of a given morphology and type of nucleation.  $K$  is the crystallization rate constant and is temperature dependent,  $n$ , an integral, is the Avrami index and contains information on nucleation and growth geometry. [20]

	Crystallization mechanism	Avrami constant		Restrictions
		K	n	
Spheres	Sporadic	$2/3 \pi g^3 l$	4	3d
	Predetermined	$4/3 \pi g^3 L$	3	3d
Discs	Sporadic	$\pi/3g^2 l d$	3	2d
	Predetermined	$\pi g^3 L d$	2	2d
Rods	Sporadic	$\pi/4 g l d^2$	2	1d
	Predetermined	$1/2 \pi g L d^2$	1	2d

Tab. (1) The Avrami parameters for crystallization of polymers [21]

However, the interpretation of the Avrami index is not straightforward because its determination can be influenced by many factors, like volume change due to phase transformation, annealing, incomplete crystallization or different mechanisms involved during the process. [20]

### 2.1.2 Keith-Padden Kinetics of Spherulic crystallization

Although Avrami Equation provides useful data of the overall kinetics of crystallization, it provides only little peek to the molecular organization of the crystalline regions and spherulites. Rate of growth of the spherulite in the radial direction is constant until the spherulites meet. After then, atactic components, impurities etc. become trapped in the interlamellar regions. Theory developed by Keith and Padden says, that a parameter of major significance is the quantity  $\delta$

$$\delta = D/G \quad (3)$$

where D is the diffusion coefficient for impurity in the melt and G represents the radial growth. The quantity  $\delta$  determine the lateral dimension of the lamellae and that non-crystallographic branching should be observed when d becomes small enough to be commensurate with the dimensions of the disordered regions on their surfaces. Thus  $\delta$  is a measure of the internal structure of the spherulite, or its coarseness. [21]

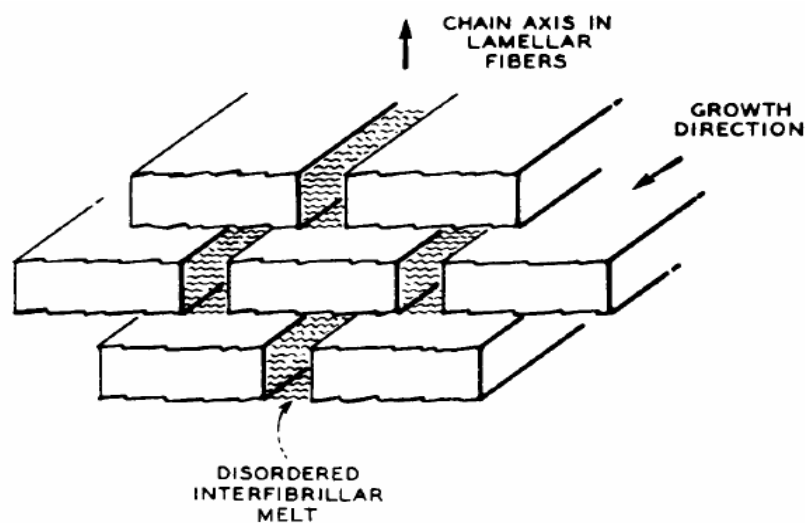
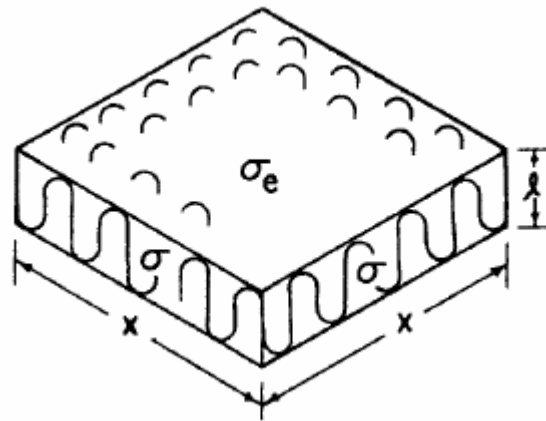


Fig. (8) Schematic representation of the distribution of residual melt and disordered material among lamellae in spherulite[21]

According to Keith and Padden, diffusion is the controlling factor at low temperatures, whereas at higher temperatures the rate of nucleation dominates. Between these two extremes the growth rate passes through a maximum where the two factors are approximately equal in magnitude. [21]

### 2.1.3 Hoffman's nucleation theory

The major shortcoming of the Keith–Padden theory resides in its qualitative nature. Although great insight into the morphology of spherulites was attained, little detail was given concerning growth mechanisms, particularly the thermodynamics and kinetics of the phenomenon.[21] Hoffman assumed that chain folding and lamellar formation are kinetically controlled, the resulting crystals being metastable. The thermodynamically stable form is the extended chain crystal, obtainable under high pressure.



*Fig. (9) Thin chain-folded crystal showing  $\sigma$  and  $\sigma_e$ . [21]*

We can see basic model illustration at fig. (9), where  $l$  is the thickness of the crystal,  $x$  is the large dimension,  $\sigma_e$  is the fold surface interfacial free energy and  $\sigma$  is the lateral surface interfacial free energy. Crystal is folded from one chain. The free energy of formation of a single chain-folded crystal may be set down in the manner of Gibbs as:

$$\Delta_{G_{crystal}} = 4xl\sigma + 2x^2\sigma_e - x^2l(\Delta f) \quad (4)$$

Where  $\Delta f$  represents the bulk free energy of fusion, which can be approximated from entropy of fusion  $\Delta S_f$ , if we assume that heat of the fusion  $\Delta h_f$  does not depend on temperature.

Then:

$$\Delta f = \Delta h_f - T \Delta S_f \quad (5)$$

## 2.2 Models of non-isothermal crystallization

During the non-isothermal crystallization, the cooling rate commonly stays constant, i.e. does not change during the process. Temperature – time relations can be described by the following equation:

$$T_{(t)} = T_i - \Omega_{(t)} \quad (6)$$

Where  $T_i$  is the initial temperature and  $\Omega_{(t)}$  is a function of time, which can be further described as  $\Omega_{(t)} = X_{(t)}$  where  $X = dT/dt$  is the cooling rate. [20]

The mechanism of phase change is strongly dependent on the cooling rate. The higher the cooling rate is, the nuclei occur at a lower temperature. [20]

### 2.2.1 Ziabicki's equation

The majority of the formulations for non-isothermal crystallization is based on the Avrami equation. Ziabicki, in his first attempt to model the dynamic crystallization, proposed that the non-isothermal crystallization can be viewed as a sequence of isothermal steps. Few prerequisites are set to express the non-isothermal crystallization by equation (7). These prerequisites are, that the nucleation and growth of the crystals are governed by thermal mechanisms only, that their time dependence comes from a change in external conditions and that the Avrami exponent is constant throughout the whole process.

$$E_{(t)} = \ln 2 \left( \int_0^t \frac{ds}{\tau_{1/2}} \right)^n \left[ 1 + a_1 \int_0^t \frac{ds}{\tau_{1/2}} + a_2 \left( \int_0^t \frac{ds}{\tau_{1/2}} \right)^2 + a_3 \dots \right] \quad (7)$$



Where  $\tau_{1/2}$  is observable half-time of crystallization,  $a_1, a_2, \dots, a_n$  are the coefficients of the series,  $n$  is the Avrami exponent and  $s$  is the time required for nucleation of the crystals. When  $a_1 = a_2 = \dots = a_n = 0$ , equation (7) becomes:

$$E_{(t)} = \ln 2 \left( \int_0^t \frac{ds}{\tau_{1/2}} \right)^n \quad (8)$$

Equation (8) can be used when the ratio between nucleation and growth rates is constant with the time and athermal nucleation is negligible. Drawback of this theory is that it can be used only in the range of temperatures where isothermal crystallization data are available. [20]

### 2.2.2 Nakamura's equation

Nakamura and coworkers assumed isokinetic conditions and derived following equation.

$$X_{(t)} = 1 - \exp \left[ - \left( \int_0^t K'(T) d\tau \right)^n \right] \quad (9)$$

Where  $n$  is the Avrami constant index determined from isothermal crystallization and  $K'$  is related to the Avrami constant  $K$  through the equation (10)

$$K' = K^{1/n} \quad (10)$$

Disadvantage of the Nakamura's model is that it does not consider the effect of the induction time. However, non-isothermal induction times can be calculated from isothermal ones by using equation:

$$t_I = \int_0^{t_{ni}} \frac{dt}{t_i(T)} \quad (11)$$

Where  $t_i(T)$  is the isothermal induction time and  $t_i$  is a dimensionless index of induction time [20]

### 2.2.3 Ozawa's equation

Ozawa accounted for the effect of cooling rate  $X$  on dynamic crystallization by properly modifying the Avrami equation. This method can be used when crystallization occurs at a constant cooling rate. The degree of conversion at temperature  $T$ ,  $X(T)$ , can be calculated as:

$$-\ln[1 - X(T)] = \frac{K^*(T)}{X^n} \quad (12)$$

where  $X$  is the cooling rate,  $n$  is the Avrami exponent and  $K^*$  is the cooling crystallization function and is related to the overall crystallization rate and indicated how fast crystallization occurs. The most interesting feature of the Ozawa's theory is the possibility to compare results of crystallization during continuous cooling with results obtained by means of Avrami equation under isothermal conditions. [20]

### 2.2.4 Experimental observation on isotactic poly-1-butene

Silvestre et al. investigated non-isothermal crystallization process of isotactic poly(1-butene) and its blends with an amorphous oligomer, the hydrogenated oligo-cyclopentadiene (HOCP). The samples were melted at 160 °C for 10 minutes and then cooled to 20 °C at different cooling rates: 0.5, 1, 2, and 4 °C/min. The morphology of crystallized samples was characterized by the presence of small and large spherulites. Two kind of spherulites grew from heterogeneous nuclei, having different activation energies. This occurs at cooling rate 4 °C/min. Nucleation of both nuclei was delayed by the addition of HOCP. That means that in the blends higher undercooling is need to heterogeneous nuclei become active. Experimental data were analyzed with Ozawa and Ziabicky theories. The Ozawa equation was satisfactorily used to describe the dynamics of the solidification of all the samples. The Avrami exponent was close to 3 for all samples (pure poly(1-butene) and blends) when it was calculated with Ozawa method. The use of Ziabicki theory did not give good agreement with experimental results. It was found that zero-order approximation did not describe the non-isothermal crystallization in poly-1-butene. [20]

### 3 USED METHODS OF ANALYSIS

#### 3.1 Polarized light microscopy

Light microscopy is very old method of observing a structure, shape, morphology of material and many others properties. Principle of this method is very simple. Microscope is as device which contains numerous magnifying lenses to achieve optical magnitude of the observed specimen. These lenses are in objective and ocular of the microscope. Also, condenser lens is needed. Its role is to convert a beam of light from tube shape to cone shape and thus illuminate a specimen in the microscope.

To achieve a polarized light, polarization filter is need. Plane polarized light is light of a single vibrational direction which is perpendicular to the direction of propagation. To obtain plane polarized light, white light is passed through a polarizing filter. It can be thought of as a ticket going through a slot. Only the ticket which is oriented in the same direction as the slot will pass through. Likewise only light of the proper vibrational direction will pass through the polarizing filter. [22]

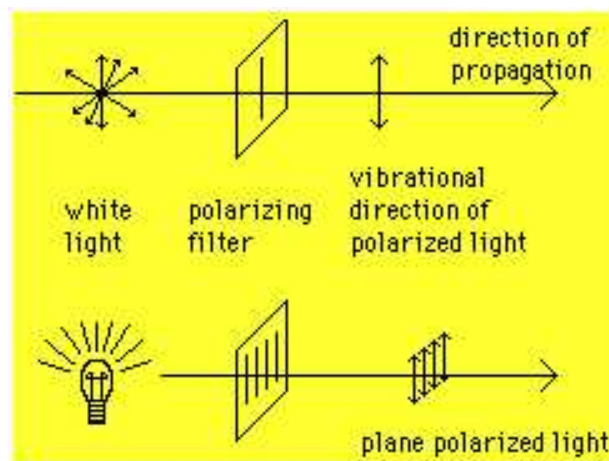


Fig. (10) Basic scheme of polarized light [22]

### 3.2 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) is important and very often used method of thermal analysis. By using DSC on polymer materials, we can determine melting point temperature, glass transition temperature, degree of cure and heat of diffusion etc. Calorimeter accepts polymer in any form (powder, pellets, fibers, fragments etc.) and weight of few milligrams is enough to perform measurement. Sample is inserted into aluminum pan and crimped by crimping press to ensure good closure of pan and good thermal contact. [23]

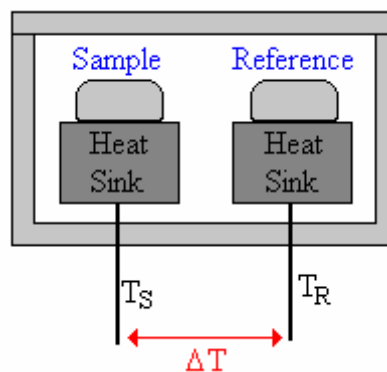


Fig. (11) Common principle of DSC [24]

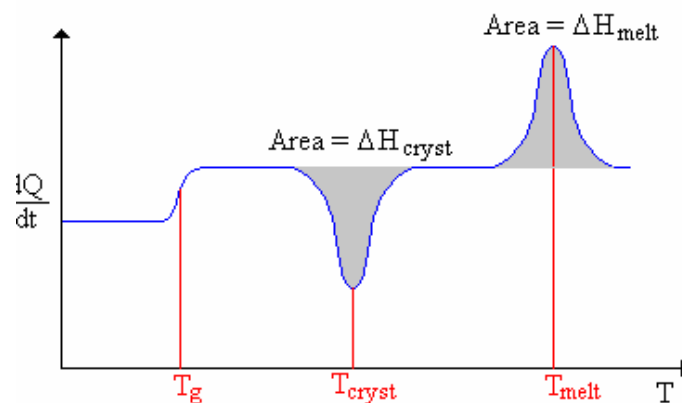
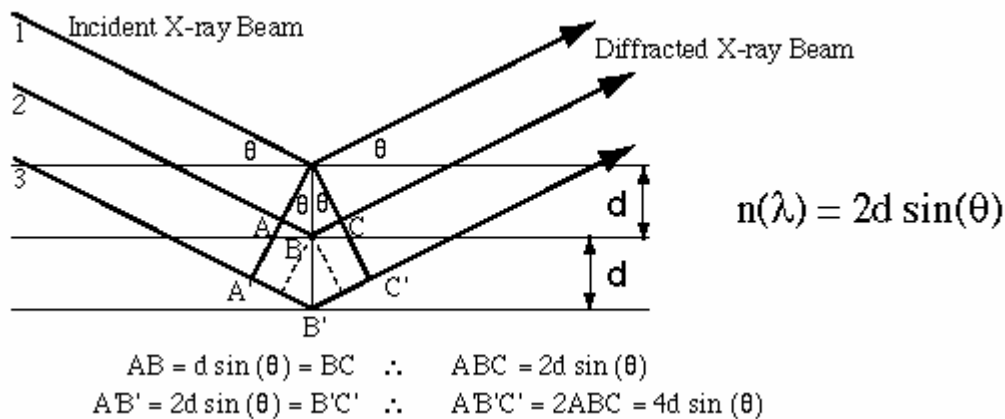


Fig. (12) Example of the DSC thermogram [24]

### 3.3 X-Ray diffraction

X-Rays are used to determine arrangement of atoms in crystals. By considering crystals as a reflection grating for X-Ray, Bragg derived his equation for distance between successive identical planes of atoms in the crystal.[21]



*Fig. (13) Bragg's Law [25]*

Intensity of the X-Ray diffraction is depends on the number of electrons involved, thus is proportional to the density. Besides Bragg diffraction lines, there is an amorphous halo caused by the amorphous phase in the polymer. The amorphous halo is broader than the corresponding crystalline peak, because of the molecular disorder. This method is called WAXS (Wide Angle X-Ray Scattering). [21]

### 3.4 Density measurement

Density of solid materials can be measured by using common laboratory scales with added device for solidity measurement. Sample is weighted in common way and then is weighted in liquid. As a liquid I used mixture of water an ethanol. Basic principle of measurement is difference between weight of the sample and sample submerged in liquid, which is relieved by upward force of the liquid. Then we can evaluate the solidity of measured sample by using following formula:

$$\rho = \frac{m_a \times \rho_f}{m_a - m_f} \quad (13)$$

Where  $\rho$  is density of the sample,  $m_a$  is the weight of the sample on the air,  $m_f$  is weight of the sample in measurement fluid and  $\rho_f$  is a density of the measurement fluid.

Solidity was measured at each of the sample prepared by pvT device. First measurement was done immediately after sample preparation and second two weeks after preparation.



*Fig. (14) Device used for solidity measurement [26]*

## **II. EXPERIMENTAL**

## 4 SAMPLE PREPARATION

### 4.1 pvT device sample preparation

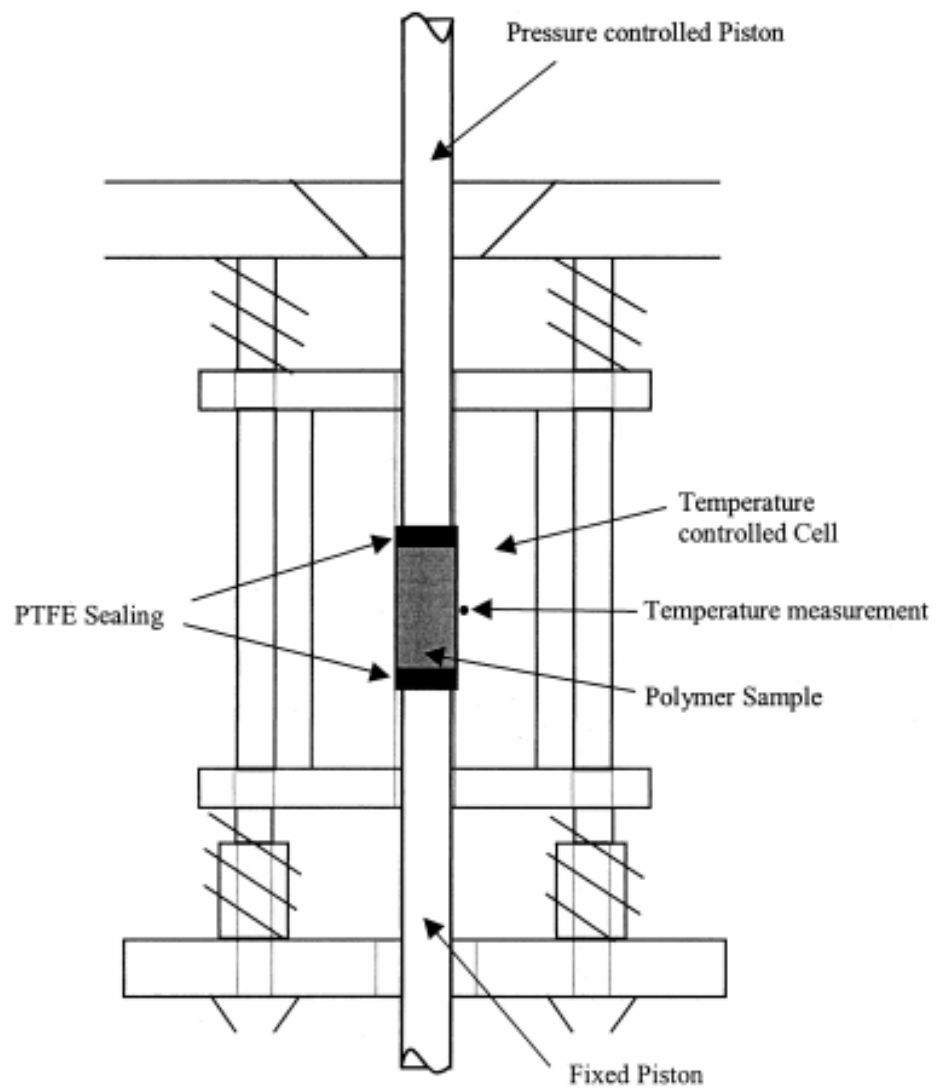
A pvT device was used to prepare samples under defined conditions (heat/cooling rate, temperature range and pressures). These samples were used to compare the obtained structures under different conditions. I used pvT100 made by SWO Polymertechnik GmbH (Krefeld, Germany)

As we can see at fig. (15), main parts of pvT device are pressure piston, fixed piston, and chamber. At the beginning of the measurement, both PTFE sealings are put into the chamber and device is calibrated to the sealings dimension. Then, approx. 0.75 g of the measured material is put into the chamber between sealings. Sample is melted under atmospheric pressure, and then is pre-compressed at pressure 40 MPa (20 MPa pre-compression at sample preparation pressure lower than 40 MPa). After these settings, the requested measurement is executed.

Diameter of the chamber is 7.8 mm. PTFE sealings are holding melt in the chamber and avoiding leak of the melt. However, during measurement of DP0401 at heating/cooling rate and temperature 220 °C, leakage of the melt appeared at pressures higher than 120 MPa. This is caused by high MFI of the DP0401.

Main disadvantage of the pvT measurement is non-accurate hydrostatic pressure on the sample in solid state. According to reference [27], the error caused by such behavior is very small and does not influence sample preparation





*Fig. (15) Scheme of pvT device [27]*

Two poly-1-butenes were examined during the experimental part, PB 0300M and DP 0401 M. Both are commercially available. They were manufactured by LyondellBasell Industries.

## DP 0401M Properties

DP 0401M			
Physical	Method	Value	Unit
Density	ISO1183	0,915	g/cm <sup>3</sup>
Melt Flow rate	ISO1183	15	g/10min
Mechanical			
Flexular Modulus	ISO 178	450	MPa
Tensile Strength at Yield	ISO8986-2	22	MPa
Tensile Strength at Break	ISO8986-2	29	MPa
Tensile Elongation at Break	ISO8986-2	300	%
Thermal			
Melting Temperature	DSC		
Tm 1		126	°C
Tm 2		114	°C

*Tab. (2) Properties of DP 0401M*

## PB 0300M Properties

PB 0300M			
Physical	Method	Value	Unit
Density	ISO1183	0,915	g/cm <sup>3</sup>
Melt Flow rate	ISO1183	4	g/10min
Mechanical			
Flexular Modulus	ISO 178	450	MPa
Tensile Strength at Yield	ISO8986-2	19,5	MPa
Tensile Strength at Break	ISO8986-2	35	MPa
Tensile Elongation at Break	ISO8986-2	300	%
Thermal			
Melting Temperature	DSC		
Tm 1		127	°C
Tm 2		116	°C

*Tab. (3) Properties of PB 0300M*

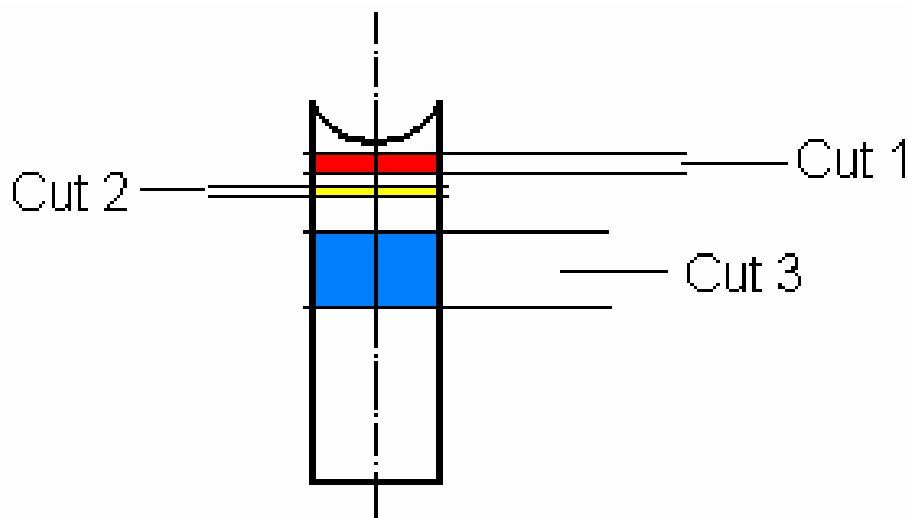
At first, complex pvT measurement was done, for pressures 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 MPa. Temperature range was from 50°C to 180°C and the cooling/heating rate was 5°C/minute. All these set of pressures were measured on one sample of polymer.

From these results, I have set a new set of pressures, which are 20, 50, 75, 100, 125, 150 and 175 MPa. For each of these newly set pressures, one sample was prepared to observe differences in structure. Then, to find influence in cooling/heating speed, complex

measurement was repeated at 1°C per minute and 50°C to 220°C temperature range. All samples were prepared at crystallization – melting – crystallization cycle.

## 4.2 Polarized light microscopy specimen preparation

Samples obtained from pvT device were in the form of cylinder with top area crumbled down, as we can see at fig. (16)



*Fig. (16) Scheme of specimens preparation from the samples*

As a first step, the top of the sample was tabulated by using microtome. Then, from area „Cut 1“, 40 µm thick plate was cut and put on the glass slide. Silicon oil was added and sample was covered with slip cover.

For polarized light microscopy, Zeis NU microscope was used. Micrographs of the observed specimens were taken by digital camera. Used magnitude for all specimens was 40x.

## 4.3 DSC specimen preparation

DSC samples were prepared from area marked as Cut 2 at fig. (16). 100µm thick pieces were cut by using microtome. After cutting from sample, specimens were cut to smaller pieces to fit into pan. Pans were made from aluminum. Weight of the specimen

was around 1mg, varying from sample to sample. Then the pans with sample were closed in crimping press.

Melting curves were measured at Instrument 2010 DSC using nitrogen inert atmosphere with flow 20ml/s.

#### **4.4 WAXS specimen preparation**

WAXS samples were prepared from area marked as Cut 3 at fig (16). Approximately 4mm thick specimens were cut by using handsaw. Then the measurement area was grinded to smooth using water grinder with very soft sand-paper. Used device was X'Pert PRO PANalytical with wavelength 1,54 Å and step size of 0,0263 °.

### **III. RESULTS AND DISCUSSION**

## 5 DSC RESULTS

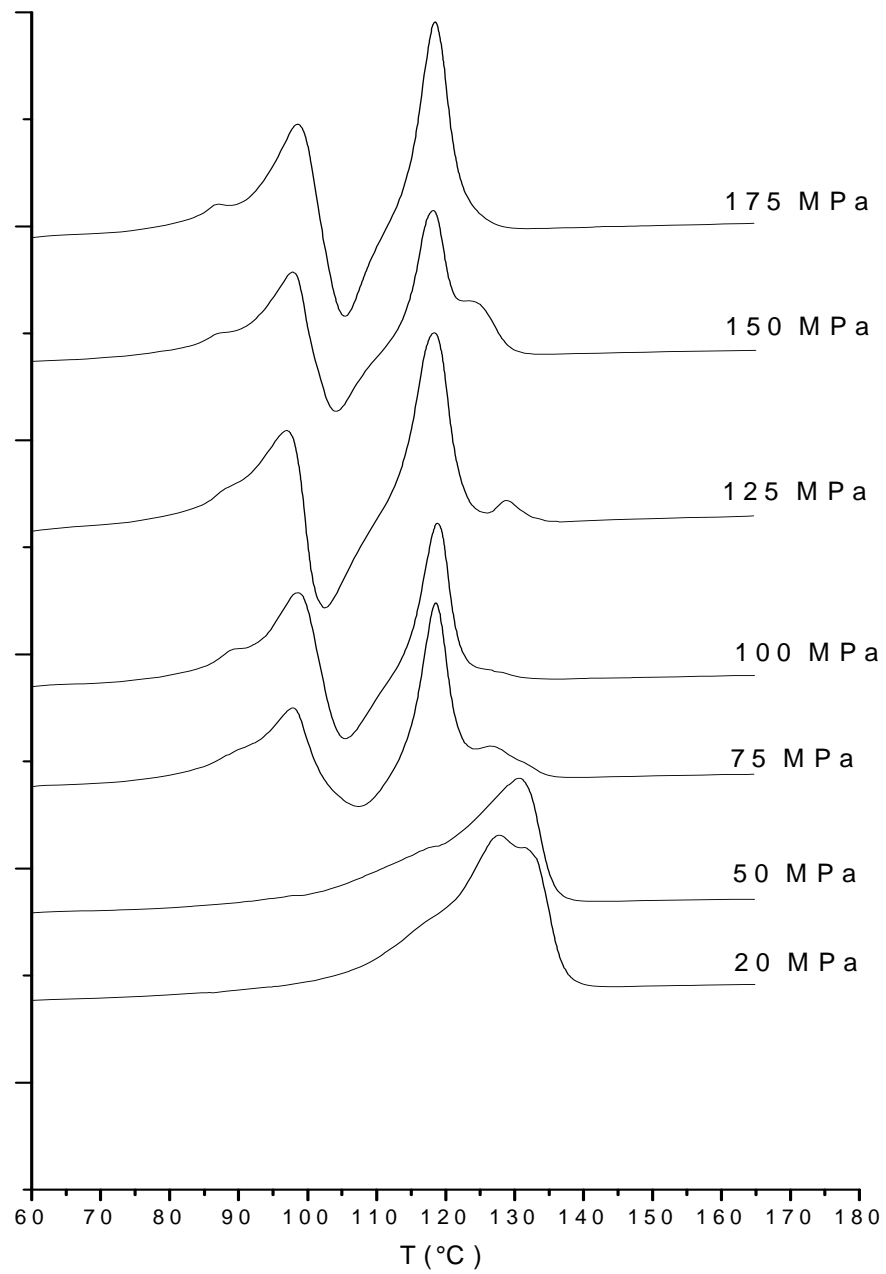


Fig. (17) DP 0401M melting curves at various crystallization pressures

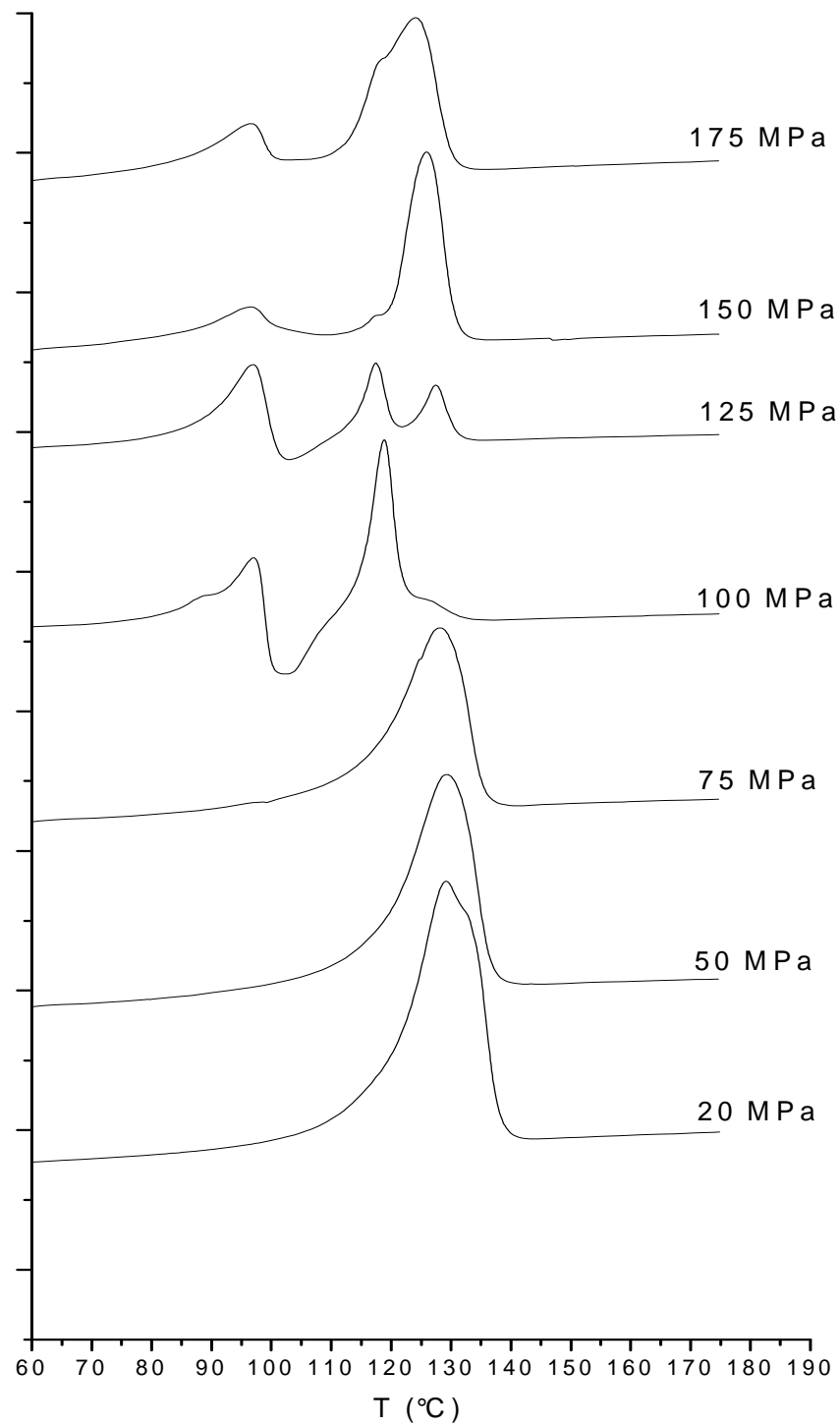


Fig. (18) PB 0300M melting curves at various crystallization pressures

### 5.1 DP 0401M DSC curves discussion

As we can see at fig.(17), for both 20 and 50 MPa crystallization pressures, phase I is shown at DSC melting curve with peaks of melting temperature at 124 °C and 133 °C respectively. With increasing pressure, 75 MPa we can assign peak at temperature of 96.5 °C to the phase I', which recrystallizes to phase II with peak at temp. 117 °C and small content of phase I is represented with peak at temp. 124 °C. With further increasing crystallization pressure from 75 to 175 MPa no significant changes are not observed except small peaks belonging to phase I which are formed after recrystallization from phase I' to phase II and phase I. From pressure 100 MPa there are present small peaks at approx 90 °C which may be assigned to phase II' or it can be also phase I' – I recrystallization. This fact can be supported by fact that X-ray spectra does not show any relevant peak of phase II but only of phase I which is also the same for phase I' [16]

Pressure of preparation (MPa)	Peak at temperature		
	Phase	Phase	Phase
	I'	II	I
20	-	-	124 °C
50	-	-	133 °C
75	96.5 °C	117 °C	124 °C
100	95.6 °C	116.7 °C	-
125	94.8 °C	115.8 °C	127 °C
150	96.1 °C	116.5 °C	123.3 °C
175	96.6 °C	116.5 °C	-

*Tab. (4) Peak temperatures of phases for preparation pressures of DP 0401M*



## 5.2 PB 0300M DSC curves discussion

Curves of crystallization pressures at 20, 50 and 75 MPa, as can be seen at fig. (18), are practically similar. All three curves have peak of phase I at 126, 125,1 and 125,9 °C respectively. Peak of phase I' is present from pressure 100 MPa to 175 MPa with significant difference. At pressure 100 and 125 MPa recrystallization exothermal peak is observed but with further increase of pressure 150 and 175 MPa it is not observed. This is completely different behavior compared to DP 0401M. Thus the material properties namely molecular weight plays important role in high-pressure crystallization behavior. At these the highest pressures is observed phase I' at 95 °C which does not recrystallize and simultaneously phase II and dominant phase I. In the tab. (5) are shown melting peaks of individual phases.

Pressure of preparation (MPa)	Peak at temperature		
	Phase	Phase	Phase
	I'	II	I
20	-	-	126 °C
50	-	-	125.1 °C
75	-	-	125.9 °C
100	94.5 °C	117 °C	124 °C
125	95 °C	116 °C	125 °C
150	94.7 °C	116 °C	122.5 °C
175	94.2 °C	116 °C	120.8 °C

*Tab. (5) Peak temperatures of phases for preparation pressures of PB 0300M*

### 5.3 Sample comparison

From the comparing of both materials (DP 0401M and PB 0300M) was found that occurrence of phase I' is function of crystallization pressure and molecular weight, because of according to producer information, both materials contains the same type of stabilizers. It would be suitable to perform these analyzes on various grades of PB-1 and compare them. DP 0401M has a lower molecular weight then PB 0300M. This could be a reason why were observed differences in appareance of phase I' at DP 0401M from crystallization pressure 75 MPa and at PB 0300M from 100 MPa. Materials also differ at recrystallization peaks where PB 0300M does not show recrystallization peaks at crystallization pressures of 150 and 175 MPa and at these pressures peaks of phase I' are much smaller compared to those at DP 0401M.

## 6 X-RAY DIFFRACTION RESULTS

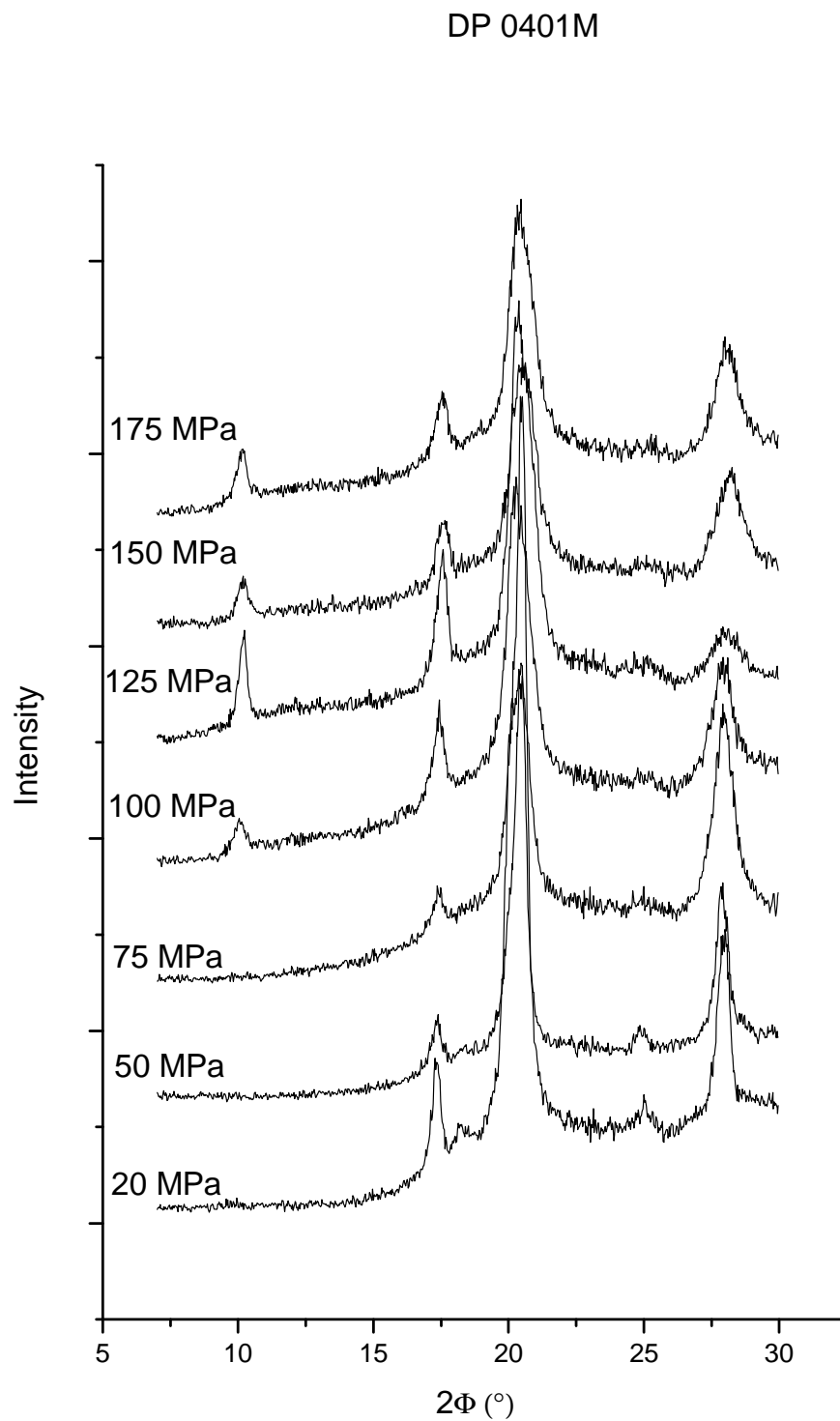


Fig. (19) WAXS curves for different pressures of preparation for DP 0401M

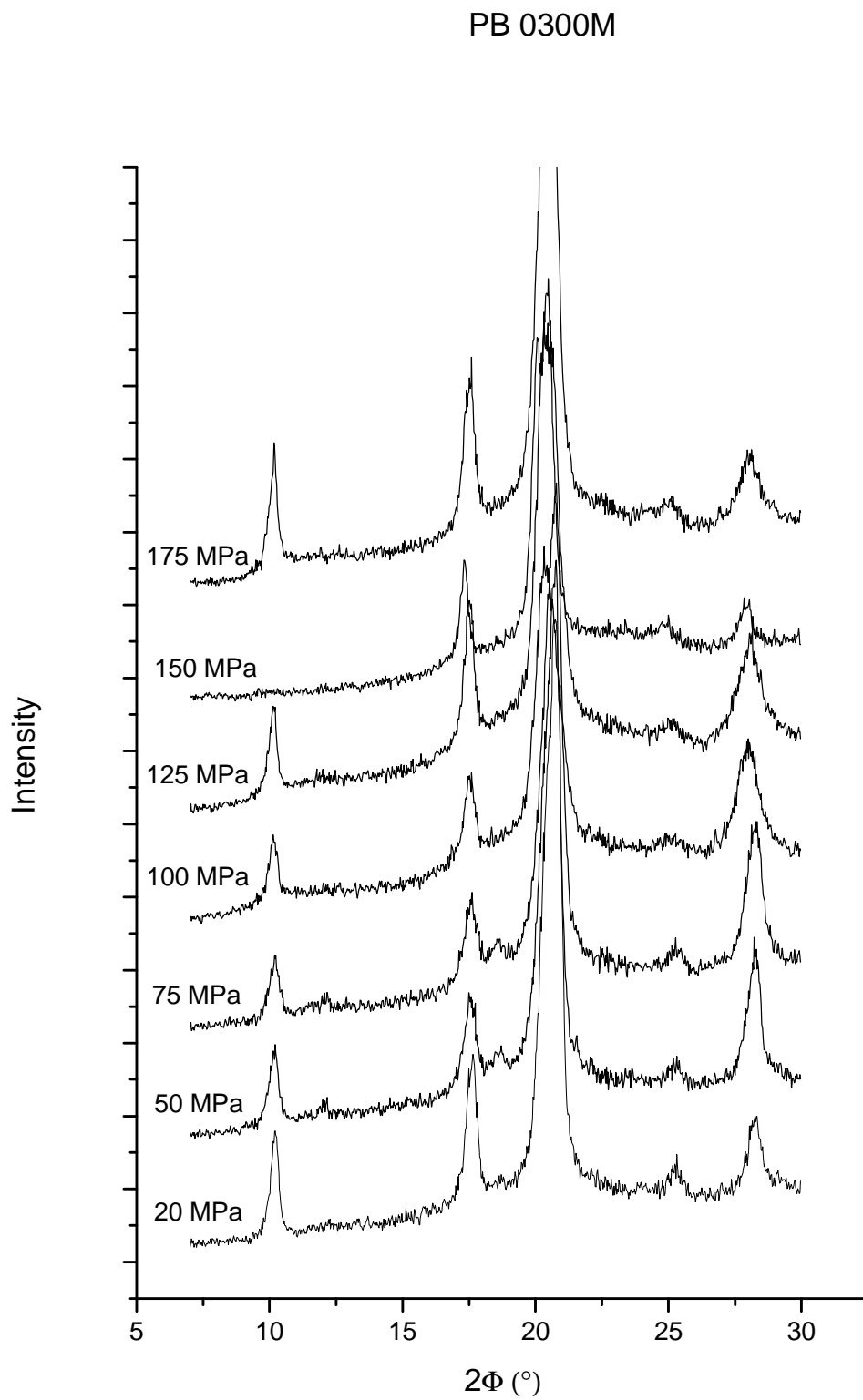


Fig. (20) WAXS curves for different pressures of preparation for PB 0300M

## 6.1 X-Ray diffraction results discussion

WAXS curves at fig. (19) and fig. (20) show almost the same pattern for both materials which corresponds to the phase I according to [16]. However, there are few differences. At some crystallization pressures and missing peak at  $8^\circ$  and  $10^\circ 2\Theta$ , which are characteristic for phase I or I', which can be probably caused by specimen preparation during cutting and polishing. Characteristic peaks of phase II at  $11,5^\circ 2\Theta$  are not observed. However, there is a peak at  $28^\circ 2\Theta$  occurring in all patterns of various pressures, which was not described in any literature and thus we can assume whether it belongs to some interferences from sample preparation or effect of the high pressure. It should also be noted that X-Ray diffraction is not able to differ a phase I and phase I' in poly-1-butene. Identification of these phases can be done by thermal analyzes as is DSC

## 7 DENSITY MEASUREMENT RESULTS

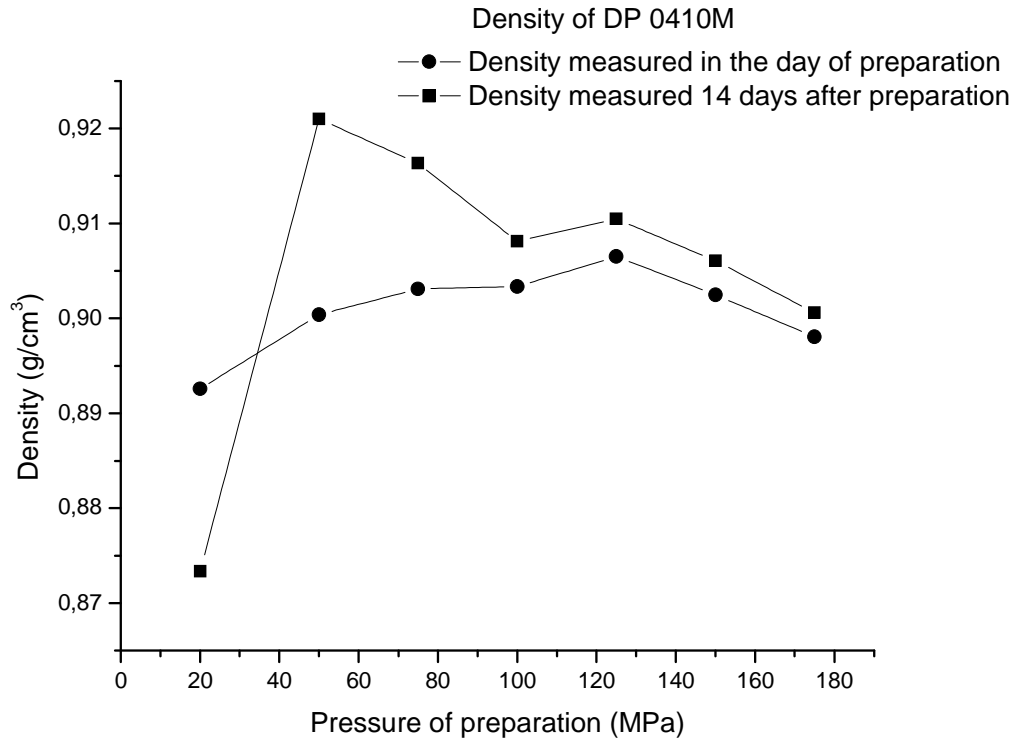
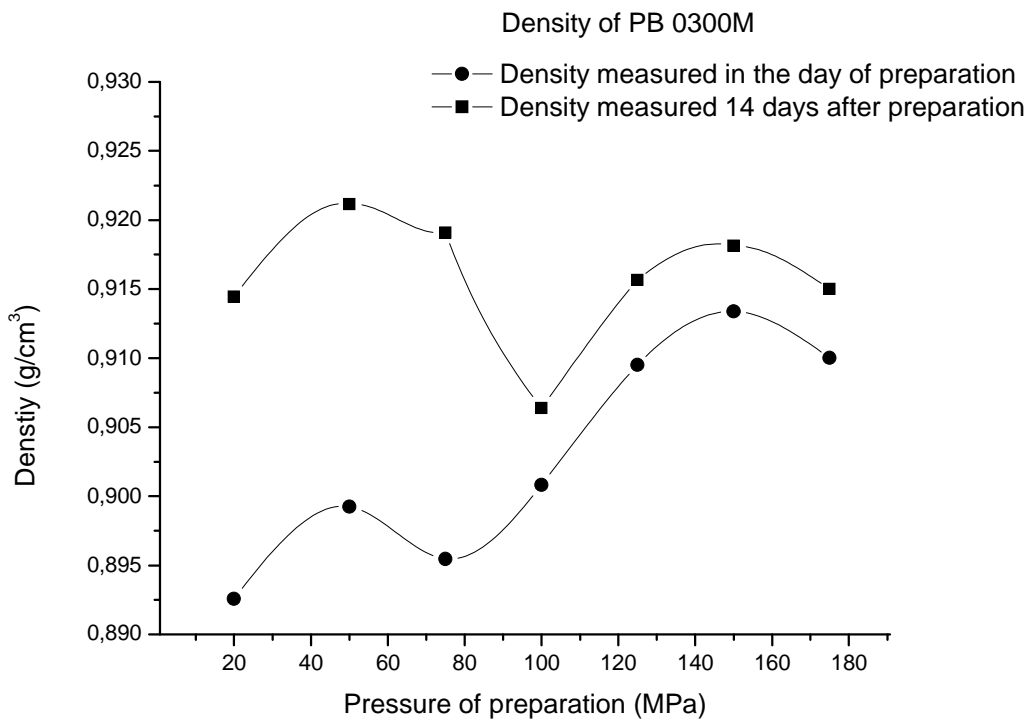


Fig. (21) Density of DP 0401M in day of preparation and 14 days after preparation



*Fig. (22) Density of PB 0300M in day of preparation and 14 days after preparation*

## 7.1 Density measurement results discussion

In both fig. (21) and fig.(22) we can see that density increased after 14 days from preparation except the lowest pressure at DP 0401 which may be measurement error, because of density of poly-1-butene increases during time after preparation. [10]

Both fig. (21) and fig. (22) show that at pressure of preparation 100MPa and higher, the increase of the density is much lower than at pressure of preparation lower than 100MPa. This could be caused by different phase I, II and I' content in dependence on crystallization pressure. Lower density change means lower shrinkage after preparation at high pressure. Thus, these findings could be used in industry during manufacturing of PB-1 products.

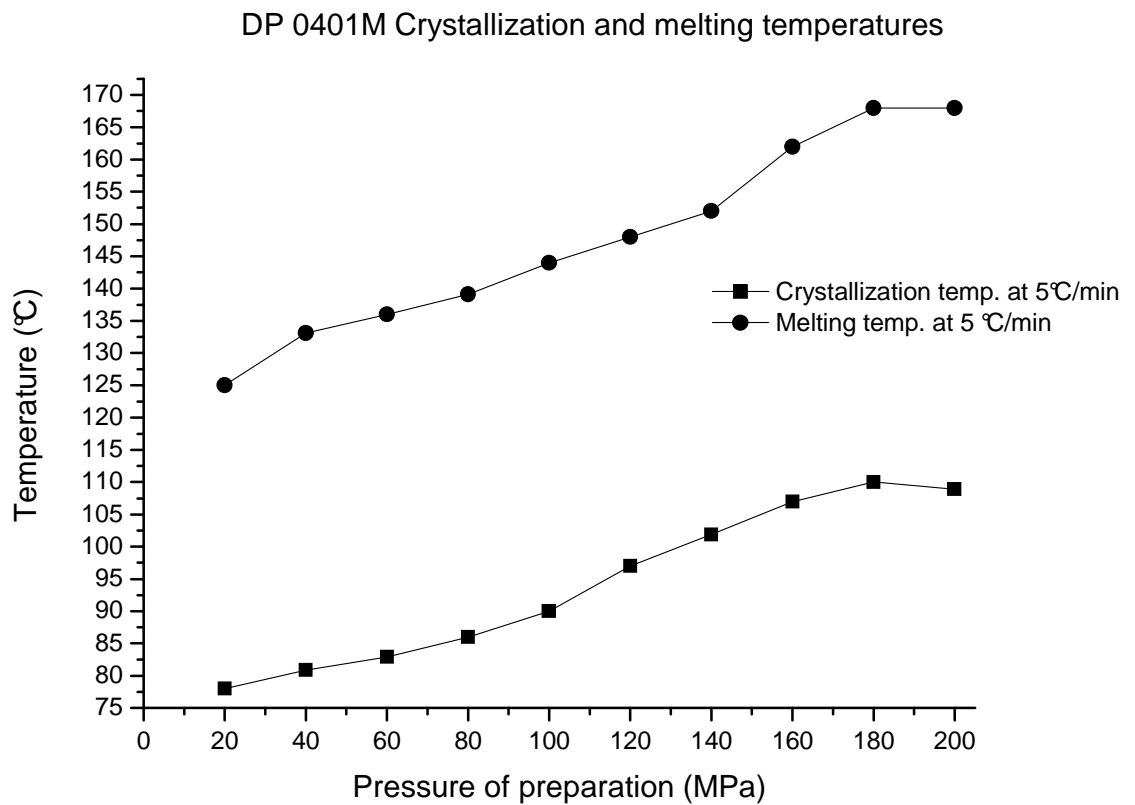
Pressure of preparation (MPa)	Density increase in %	
	DP 0401M	PB 0300M
20	-	3.2
50	2.3	2.2
75	1.5	2.1
100	0.5	0.6
125	0.4	0.7
150	0.4	0.5
175	0.3	0.6

*Tab. (6) Increase of density in percentage*

## 8 PVT SAMPLE MEASUREMENT RESULTS

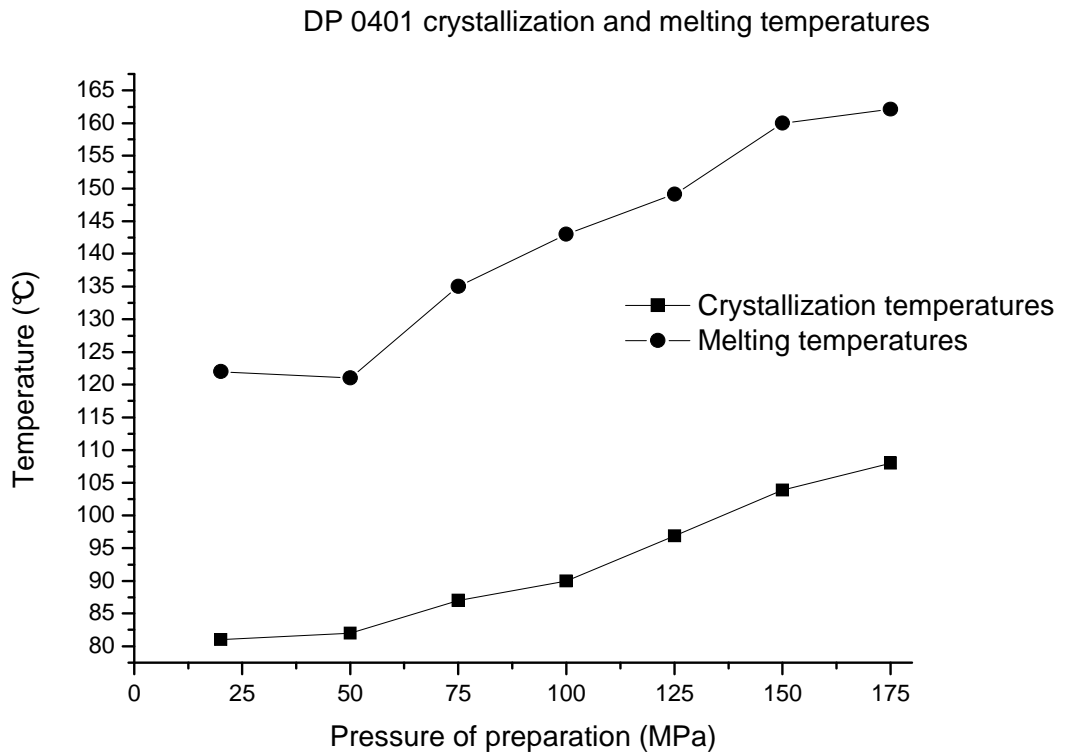
Data from each sample measurement were mathematically analyzed. Temperatures of crystallization and melting were captured at mid-point of the curve and printed in following figures and tables.

### 8.1 DP 0401M crystallization and melting temperatures



*Fig. (23) DP 0401M crystallization and melting temperatures analyzed from overall measurements of the material*





*Fig. (24) DP 0401M crystallization and melting temperatures analyzed from sample preparation at 5°C/min*

As we can see at fig. (23), both crystallization and melting temperatures at 5°C/min are increasing with increasing pressure of preparation. Also, melting temperatures could not be measured due to error of the used pvT device.

Data acquired from sample preparation at fig. (24) shows increasing temperatures, for both crystallization and melting, with higher pressure. Only exception is melting temperature at 50 MPa, which is slightly lower than temp. at 20 MPa.

Pressure of preparation (MPa)	Sample preparation		Pressure of preparation (MPa)	Overall material measurement			
				5°C/min		1°C/min	
	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)		T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
20	81	122	20	78	125	-	-
50	82	121	40	80.9	133.1	-	-
75	87	135	60	82.9	136	-	-
100	90	143	80	86	139.1	-	-
125	96.9	149.1	100	90	144	-	-
150	103.9	160	120	97	148	-	-
175	108	162.1	140	101.9	152	-	-
			160	107	162	-	-
			180	110	168	-	-
			200	108.9	168	-	-

Tab. (7) Summary of crystallization and melting temperatures of DP 0401M

### 8.2 PB 0300M crystallization and melting temperatures

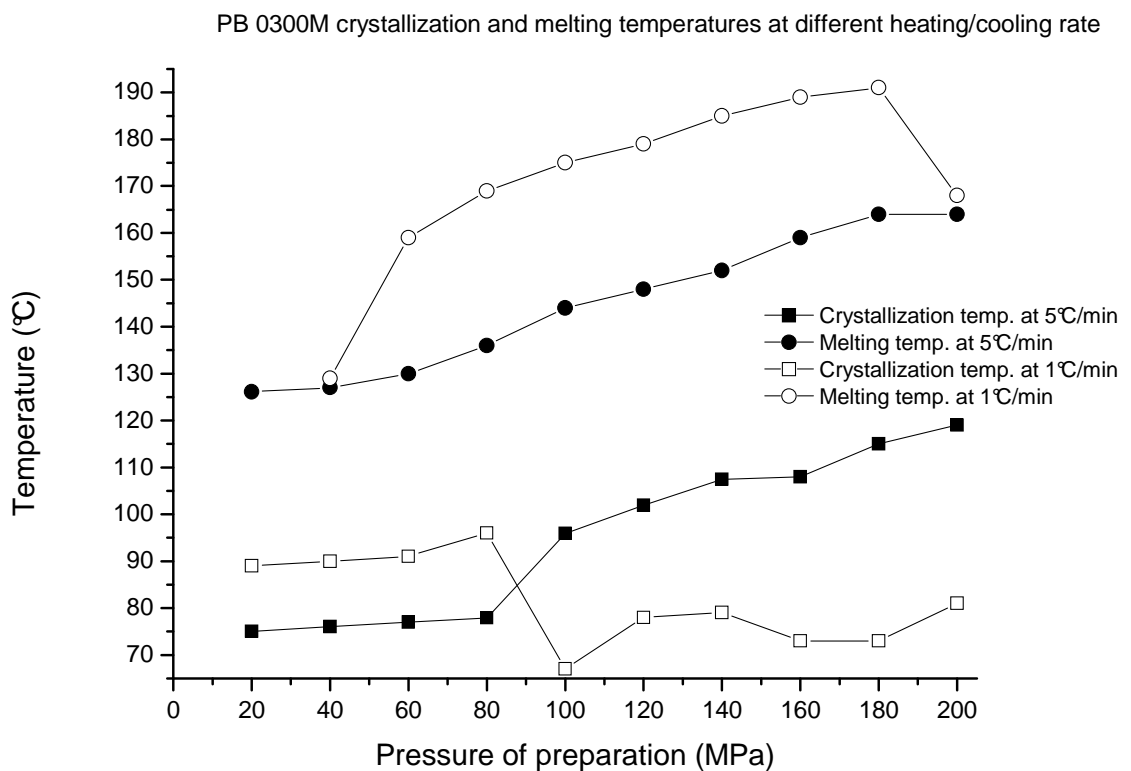
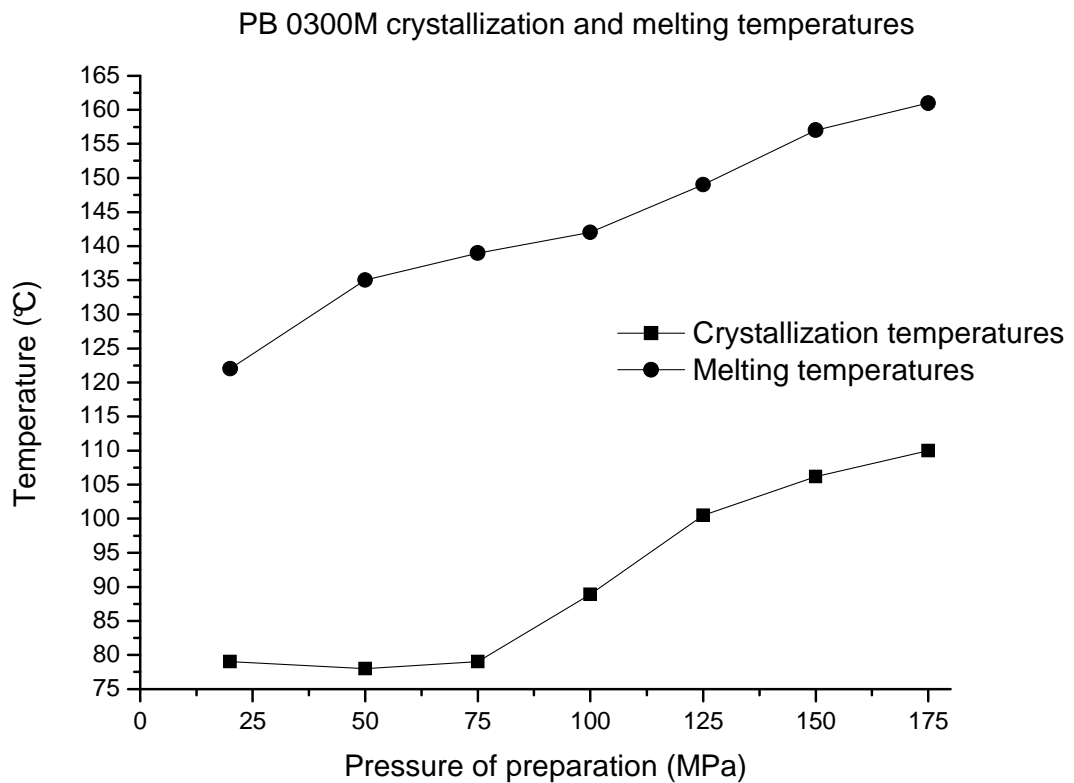


Fig. (25) PB 0300M crystallization and melting temperatures analyzed from overall measurements of the material at different cooling/heating rate



*Fig. (26) PB 0300M crystallization and melting temperatures analyzed from sample preparation at 5 °C/min*

Increasing crystallization and melting temperatures at heating/cooling rate 5 °C/min are shown in fig. (25), in pressure dependency. But at heating/cooling rate 1 °C/min, crystallization temp. is increasing up to 80 MPa, then it drops rapidly and shows random pattern of temperature change. Melting temperature at 1 °C/min drops rapidly after pressure 180 MPa, before this pressure it follows increasing trend with a higher pressure. This is possible incorrect measurement. Melting temp. at 20 MPa for 1 °C/min is missing due to influenced sample by previous thermal history.

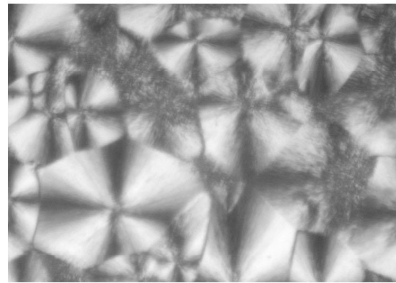
Pressure of preparation (MPa)	Sample preparation		Pressure of preparation (MPa)	Overall material measurement			
				5°C/min		1°C/min	
	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)		T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)
20	79	122	200	75	126.1	89	-
50	78	135	400	76	127	90	129
75	79	139	600	77	130	91	159
100	88.9	142	800	77.9	136	96	169
125	100.5	149	1000	95.9	144	67	175
150	106.2	157	1200	101.9	148	78	179
175	110	161	1400	107.5	152	79	185
			1600	108	159	73	189
			1800	115	164	73	191
			2000	119	164	81	168

*Tab. (8) Summary of crystallization and melting temperatures of PB 0300M*

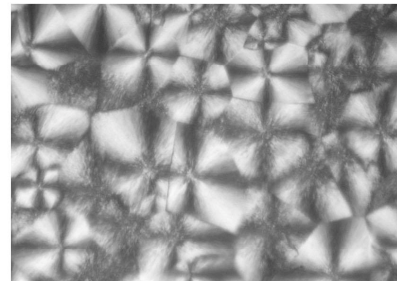
### 8.3 Temperatures anomalies discussion

One of the possible reasons for decreasing temperatures at higher pressures could be a low heat conduction of the polymer. When the sample is melted on the contact with the cell, core of the sample still could have lower temperature and thus some percentage of unmelted crystals. This can clarify an anomaly at fig. (26). But anomaly occurs more often at lower heating/cooling rate, when effect of the low heat conduction could not have a place due to long times of heating/cooling, giving a sample enough time to melt/crystallize completely. Anomaly could be caused by a recrystallization during a melting at low heating/cooling rates and thus possible phase II' to phase I' transformation could occur.

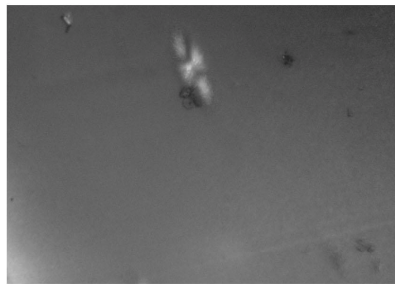
## 9 POLARIZED LIGHT MICROSCOPY RESULTS



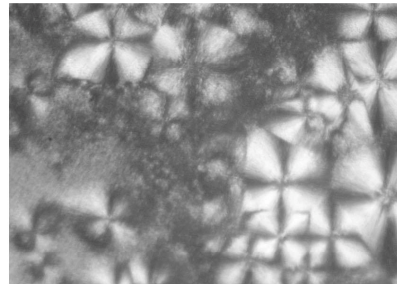
20 MPa



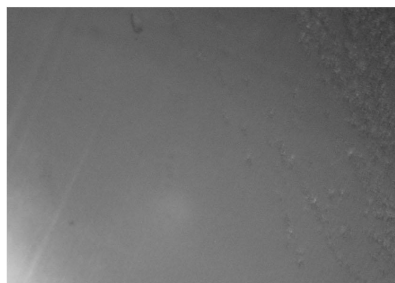
50 MPa



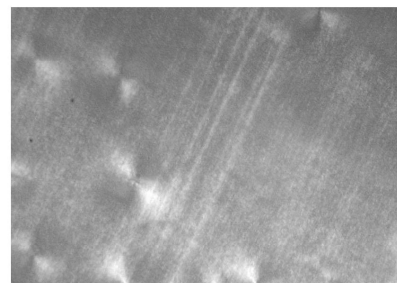
75 MPa - edge



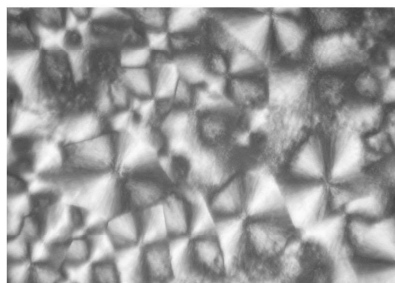
75 MPa - core



100 MPa - edge



100 MPa - core



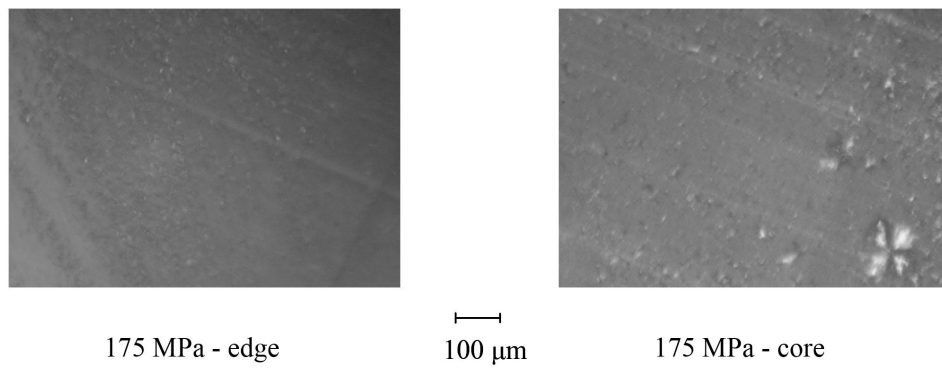
125 MPa



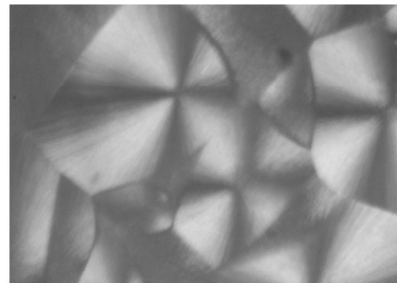
150 MPa

—  
100 μm

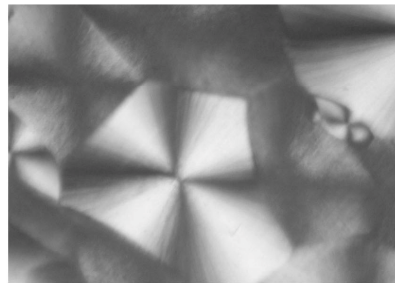
*Fig. (27) DP 0401 samples morphology, part A*



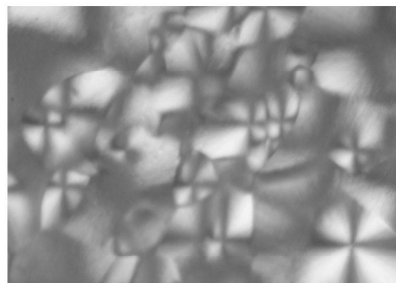
*Fig. (28) DP 0401 sample morphology, part B*



25 MPa



50 MPa



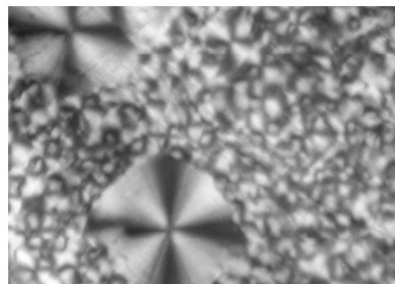
75 MPa



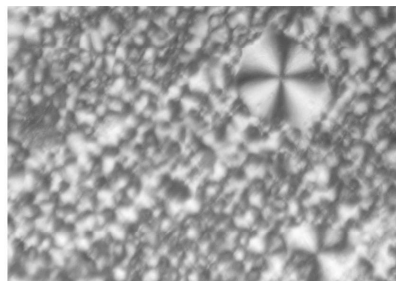
100 MPa



125 MPa



150 MPa



175 MPa

—  
100  $\mu\text{m}$

*Fig. (29) PB 0300M samples morphology*

Morphology of DP 0401 can be seen in fig. (27) and fig. (28) For pressures 20 and 50 MPa, spherulitic structure is observed with typical Maltese crosses. These samples contain only phase I. For pressure 75 MPa, edge of the specimen does not show any visible Maltese crosses but in the core of the sample they can be found. This is the first sample at DP 0401M which contains phase I'. Difference between core and edge of the sample could be an effect of the low heat conduction of the polymer. Photos of the pressure of preparation 100 MPa show similarities as at 75 MPa. However, very small spherulites can be seen in close distance from the edge. Maltese crosses can be found in the core of the sample. Morphology of samples with pressure of preparation 125 MPa is very similar to those prepared at 20 and 50 MPa. There are no differences at core and edge of the sample and Maltese crosses are found on every part of the sample. Sample prepared at 150 MPa shows structure with low number of Maltese crosses scattered across the sample and high number of small spherulites, again scattered across the sample. For pressure of preparation 175 MPa, there is again a difference between edge and core of the sample. Spherulites can be found only in the core of the sample and small crystals are scattered over the whole sample. According to [28], morphology of samples prepared at 75 and 150 MPa is typical for a poly(1-butene). Also, the crystallization temperature and cooling rate have an impact to the morphology of the samples. This fact combined with a low heat transition of the polymers could lead to a state, where crystallization temperature is dependent to a place in the sample.

When we compare a WAXS results with morphology of each sample, there is no reliable interrelation between them.

Morphology of PB 0300M is shown at fig. (29). Samples prepared at 20 and 50 MPa shows almost the same morphology, with Maltese crosses of the spherulites all over the sample. At pressure of preparation 75 MPa, structure is combined with large spherulites with small ones between them. Small crystalline structure can be seen at sample prepared at 100 MPa, with few large spherulites scattered over the sample. Structure of sample prepared at 125 MPa shows combination of large and small spherulites. Both samples prepared at 150 and 175 MPa shows almost the same structure, large number of very small



crystals with few big spherulites scattered over the sample. Appearance of small and large crystals in one sample could be explained by changing rate of cooling during crystallization process. We could also see that at higher pressure where number of large spherulites is significantly lower.

As written above, again no connection between WAXS and morphology was observed.

When we compare morphology of DP 0401M with DSC results, with first appearance of phase I' at DSC, difference between core and edge of the sample occurs. This could be caused by lower molecular weight of the DP 0401M. Samples prepared at 125 MPa however show no difference between edge and core. This could be caused by combination of changing cooling rate, molecular weight and pressure.

PB 0300M shows combination of small quantity of large crystals and large number of small crystals after appearance of phase I' at DSC curve, which is above 75 MPa. Samples prepared at 20,50 and 75 MPa shows mostly large spherulites in the structure. When both structures are compared, DP 0401M have smaller crystals at same pressure than the PB 0300M.

## CONCLUSION

This work describes results of high-pressure, non-isothermal crystallization of two homopolymers of isotactic poly(1-butene) with different molecular weights and reveals relations between molecular weight, cooling rate and phase composition.

DSC proves that appearance of phase I' is dependant on pressure of crystallization and molecular weight of the poly(1-butene). According to DSC scan, phase I' occurs at lower pressure in poly(1-butene) with lower molecular weight. For DP 0401M(lower molecular weight) it is at 75 MPa, for PB 0300M(higher molecular weight) at 100 MPa. PB 0300M curves show no recrystallization peaks at 150 and 175 MPa and smaller peaks for phase I'.

WAXS curves prove that there is no phase II in measured samples and all phase II peaks at DSC curves are caused by recrystallization during measurement. However, X-Ray diffraction cannot distinguish between phase I and phase I'

Solidity measurement revealed that with increasing pressure the density increase is lower. Samples crystallized at 50 MPa have density increase more than 2%, samples crystallized at 1750 MPa have density increase 0,3-0,6%. Lower solidity increase means lower shrinkage after aging and that fact could be used during manufacturing of the products made from poly(1-butene).

Crystallization and melting temperatures, which were analyzed from crystallization and melting curves obtained by pVT during sample preparation, are increasing with increasing pressures. However, few anomalies have been found. PB 0300M shows crystallization pressure decrease after 80 MPa and follows random pattern. When we compare this fact with DSC curves, we can found that drop of the crystallization pressure could be caused by appearance of phase I'. This anomaly occurs at rate of cooling 1°C/min and could be caused by phase II' to phase I' transformation. Anomaly also occurs at cooling rate 5 °C/min. This could be caused by low thermal conductivity of the polymer and different cooling rate at edge and core of the sample.

Morphology revealed by polarized light microscopy shows differences between core and edge of the samples of DP 0401M. Core contains large spherulites and edge is filled with small crystals with exception of pressure 125 MPa. PB 0300M morphology shows combination of small and large crystals above 75 MPa. Both materials show change in morphology when phase I' appears. DP 0401 have different core and edge structure and PB 300M have combinations of small and large crystals. This could be caused by combination of high pressure, low heat conductivity and molecular weight. Also, heat conductivity increases with crystal appearance and this fact, together with possible influence of pressure on the heat conductivity could cause morphology which we are observing.

**REFERENCES**

- 1) J. A. BRYDSON: Plastic materials seventh edition, Butterworth-Heinemann. 1999, 899 p. ISBN 0-7056-4132
- 2) M. KASZONYIOVA, F. RYBNIKAR, P.H GEIL: Crystallization and transformation of polybutene-1, J.Macromol. Sci. Phys. 44, 2004, 1095-1114.
- 3) A. RAM: Fundamentals of polymer engineering, Plenum Press, 1997, 232 p. ISBN 0-306-45726-1
- 4) F. SCHEMM, F. VAN DE VLIET, K. KÖNNECKE, J. GRASMEDER: Polybutene-1 – Entering the next generation, Bassel, 2004
- 5) D. MARING, M. WILHELM, H. W. SPIESS, B. MEURER, G. WEILL: Dynamics in the crystalline polymorphic forms I and II and form III of isotactic poly-1-butene, J. Pol. Sci. Phys. 38, 2000, pp. 2611-2624
- 6) M.L. DI LORENZO, M.C. RIGHETTI, B. WUNDERLICH: Influence of Crystal Polymorphism on the Three-Phase Structure and on the Thermal Properties of Isotactic Poly(1-butene), Macromolecules 42, 2009, pp. 9312-9320
- 7) C. D. ROSSA, F. AURIEMMA, O. R. DE BALLESTEROS, F.ESPOSITO, D.LAGUZZA, R. DI GIROLAMO, L. RESCONI: Crystallization properties and polymorphic behavior of isotactic poly(1-butene) from metallocene catalysts: The crystallization of form I from the melt, Macromolecules 42, 2009, pp. 8286-8297
- 8) M. KASZONYIOVA, F. RYBNIKAR, P.H GEIL: Polymorphism of isotactic poly(1-butene), J. Macromol. Sci. Phys. 44, 2005, 377-396.
- 9) WHITE, JAMES L., CHOI, DAVID D. : Polyolefins – processing, structure development and properties, 2005, 271 p. ISBN 978-1-56990-369-8
- 10) S.KOPP, J. C. WITTMANN, B. LOTZ: Phase II to phase I crystal transformation in polybutene-1 single crystals: a reinvestigation, J. Mat. Sci. 29, 1994, pp. 6159-6166
- 12) M.L. DI LORENZO, M.C. RIGHETTI: The three phase structure of isotactic poly(1-butene), Polymer 49, 2008, pp. 1323-1331.

- 13) M. TOSAKA, T. KAMIJO, M. TSUJI, S. KOHJIYA, T. OGAWA, S. ISODA, T. KOBAYASHI: High-resolution transmission electron microscopy of crystal transformation in solution-grown lamellae of isotactic polybutene-1, *Macromolecules* 33, 2003, pp. 9666-9672.
- 14) A. MARIGO, C. MAREGA, G. CECCHIN, G. COLLINA, G. FERRARA: Phase transition II  $\rightarrow$  I in isotactic poly-1-butene: wide- and small-angle X-Ray scattering measurement, *E. Polym. J.* 36, 2000, pp. 131-136
- 15) K. W. CHAU, Y. C. YANG, P. H. GEIL: Tetragonal  $\rightarrow$  twinned hexagonal crystal phase transformation in polybutene-1, *J. Mat. Sci.* 21, 1986, pp. 3002-3014
- 16) J. COOKE, A. J. RYAN, W. BRAS: Time-resolved X-ray studies of polymorphism in isotactic polybut-1-ene, *Nuclear instruments and methods in physics research B* 97, 1995, pp. 269-272
- 17) F. AZZURRI, A. FLORES, G. C. ALFONSO, F. J. BALTA CALLEJA: Polymorphism of isotactic poly(1-butene) as revealed by microindentation hardness. 1. Kinetics of the transformation, *Macromolecules* 35, 2002, pp. 9069-9073
- 18) F. AZZURRI, A. FLORES, G. C. ALFONSO, I. SICS, B. S. HSIAO, F. J. BALTA CALLEJA: Polymorphism of isotactic polybuteneI as revealed by microindentation hardness. Part II: correlations to microstructure, *Polymer* 44, 2003, pp. 1641-1645
- 19) S. JIANG, Y. DUAN, L. LI, D. YAN, E. CHEN, S. YAN: An AFM study on the structure and melting behavior of melt-crystallized isotactic poly(1-butene), *Polymer* 45, 2004, pp. 6365-6374
- 20) M.L. DI LORENZO, C. SILVESTRE: Non-isothermal crystallization of polymers, *Prog. Polym. Sci.* 24, 1999, pp. 917-950
- 21) L. H. SPERLING: *Introduction to Physical Polymer Science*. 3rd. edition, Wiley-Interscience, 2001. 671 p. ISBN 0-471-32921-5
- 22) <http://www.sewanee.edu/chem/Chem&Art/MS/OMB/OMB.htm> 9.5.2010
- 23) T.R. CROMPTON, *Polymer reference handbook*, 2006, 704 p. ISBN 1859574920
- 24) URL <http://faculty.uscupstate.edu/llever/Polymer%20Resources/DSC.htm> available 22.4.2010

25) URL <http://www.geology.wisc.edu/courses/g360/xray992.html> available 1.5.2010

26) URL

[http://www.preciz.si/slike/trgovina/opcije/preciz\\_si\\_servis\\_in\\_prodaja\\_tehtnic\\_kern\\_abt\\_a01.jpg](http://www.preciz.si/slike/trgovina/opcije/preciz_si_servis_in_prodaja_tehtnic_kern_abt_a01.jpg), available 28.4.2010

27) L. BENÍČEK, High-pressure crystallization of polypropylene, 2005, 117p, Master thesis on TBU in Zlín, Faculty of Technology, Supervised by Ing. Martin Obadal, Ph.D.

28) Q. FU, B. HECK, G. STROBL, Y. THOMANN: A temperature- and molar mass-dependent change in the crystallization mechanism of poly(1-butene): Transition from chain-folded to chain-extended crystallization?, *Macromolecules* 24, 2001, pp. 2502-2511

**LIST OF SYMBOLS AND ABBREVIATIONS**

pV <sub>T</sub>	Pressure-volume-Temperature	
DSC	Differential scanning calorimetry	
WAXS	Wide-angle X-Ray Scattering	
PB-1	Poly(1-butene)	
PE	Polyethylene	
PP	Polypropylene	
Å	nm	Ångström
SAXS	Small-angle X-Ray Scattering	
X <sub>(t)</sub>	Crystallinity fraction	
t	s	Time
K	Constant of avrami equation	
n	Constant of avrami equation	
D	Diffusion coefficient	
G	Radial growth	
Δf	Bulk free energy of fusion	
ΔS <sub>f</sub>	Entropy of the fusion	
Δh <sub>f</sub>	Heat of the fusion	
σ <sub>e</sub>	Fold surface interfacial free energy	
T <sub>i</sub>	Initial temperature	
Ω <sub>(t)</sub>	Function of time	
τ <sub>1/2</sub>	Observable half-time of crystallization	
t <sub>i</sub> (T)	isothermal induction time	
t <sub>l</sub>	Dimensionless index of induction time	
K*	Cooling crystallization function	

---

HOCP		Hydrogenated oligocyclopentadiene
$\rho$	$\text{g/cm}^3$	Density of the sample
$m_a$	g	Weight of the sample on the air
$m_f$	g	Weight of the sample in measurement fluid
$\rho_f$	$\text{g/cm}^3$	Density of the measurement fluid.
PTFE		Polytetraflourethylen
MFI		Melt flow index



**LIST OF FIGURES**

Fig. (1) Scheme of poly(1-butene) polymerization[4] .....	13
Fig. (2) 3/1 helix packing in form I [5] .....	14
Fig. (3) Scheme of polymorphic behavior of metallocene made poly-1-butene [7] .....	15
Fig. (4) Unit cell of form III in isotactic poly-1-butene [9] .....	16
Fig. (5) Scheme of crystallization and phase transformation of poly-1-butene [13] .....	17
Fig. (6) Phase II to I transformation captured by WAXS [14].....	18
Fig. (7) Characteristics WAXS patterns for hexagonal and tetragonal forms [16].....	19
Fig. (8) Schematic representation of the distribution of residual melt and disordered material among lamellae in spherulite[21] .....	22
Fig. (9) Thin chain-folded crystal showing $\sigma$ and $\sigma_e$ . [21].....	23
Fig. (10) Basic scheme of polarized light [22] .....	27
Fig. (11) Common principle of DSC [24].....	28
Fig. (12) Example of the DSC thermogram [24] .....	28
Fig. (13) Bragg's Law [25] .....	29
Fig. (14) Device used for solidity measurement [26] .....	30
Fig. (15) Scheme of pvT device [27] .....	33
Fig. (16) Scheme of specimens preparation from the samples .....	35
Fig. (17) DP 0401M melting curves at various crystallization pressures .....	38
Fig. (18) PB 0300M melting curves at various crystallization pressures .....	39
Fig. (19) WAXS curves for different pressures of preparation for DP 0401M .....	43
Fig. (20) WAXS curves for different pressures of preparation for PB 0300M.....	44
Fig. (21) Density of DP 0401M in day of preparation and 14 days after preparation.....	46
Fig. (22) Density of PB 0300M in day of preparation and 14 days after preparation.....	47
Fig. (23) DP 0401M crystallization and melting temperatures analyzed from overall measurements of the material .....	48
Fig. (24) DP 0401M crystallization and melting temperatures analyzed from sample preparation at 5°C/min .....	49
Fig. (25) PB 0300M crystallization and melting temperatures analyzed from overall measurements of the material at different cooling/heating rate.....	50
Fig. (26) PB 0300M crystallization and melting temperatures analyzed from sample preparation at 5°C/min .....	51

---

Fig. (27) DP 0401 samples morphology, part A .....	53
Fig. (28) DP 0401 sample morphology, part 2 .....	54
Fig. (29) PB 0300M samples morphology.....	55

**LIST OF TABLES**

Tab. (1) The Avrami parameters for crystallization of polymers [21].....	21
Tab. (2) Properties of DP 0401M .....	34
Tab. (3) Properties of PB 0300M.....	34
Tab. (4) Peak temperatures of phases for preparation pressures of DP 0401M.....	40
Tab. (5) Peak temperatures of phases for preparation pressures of PB 0300M.....	41
Tab. (6) Increase of density in percentage .....	47
Tab. (7) Summary of crystallization and melting temperatures of DP 0401M.....	50
Tab. (8) Summary of crystallization and melting temperatures of PB 0300M.....	52