

HIGH-PRESSURE CRYSTALLIZATION OF POLYPROPYLENE

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Master Thesis
2005



Tomas Bata University in Zlín
Faculty of Technology

Univerzita Tomáše Bati ve Zlíně

Fakulta technologická

Ústav inženýrství polymerů
akademický rok: 2004/2005

ZADÁNÍ DIPLOMOVÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Lubomír BENÍČEK**
Studijní program: **M2808 Chemie a technologie materiálů**
Studijní obor: **Technologie kůže, plastů a pryže – GPT**

Téma práce: **Vysokotlaká krystalizace polypropylenu**

Zásady pro vypracování:

1. Vypracujte literární studii na dané téma.
2. Provedte vysokotlakou krystalizaci modifikovaných polypropylenů.
3. Vzorky zhodnoťte pomocí vhodných experimentálních metod.
4. Diskutujte dosažené výsledky.

Rozsah práce:

Rozsah příloh:

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

Seznam odborné literatury:

dle doporučení vedoucího diplomové práce

Vedoucí diplomové práce:

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Ústav inženýrství polymerů

Datum zadání diplomové práce:

7. února 2005

Termín odevzdání diplomové práce:

30. května 2005

Ve Zlíně dne 10. února 2005


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ABSTRACT

A novel crystallization method for the preparation of 3-phase crystalline systems in isotactic polypropylene has been proven. Commercially available isotactic polypropylene, Mosten 58412, was modified by a specific β -nucleation agent based on *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide (NU100). A pvT100 high-pressure unit was used for high-pressure crystallization. Neat and nucleated samples were isothermally crystallized at various pressures and various crystallization temperatures; non-isothermal crystallization was carried out using three different cooling rates under 100 MPa pressure.

Crystallization kinetics were studied from dilatometric data, the polymorphic structure was determined using wide-angle X-ray scattering, the morphology was observed by polarized light microscopy, melting behavior was studied by differential scanning calorimetry, mechanical properties represented by elastic modulus and hardness were studied using dynamic mechanical thermal analysis and Shore D measurement.

V této diplomové práci byla zkoumána nová krystalizační metoda přípravy 3-fázových krystalických systémů v polypropylen. Komerčně dostupný izotaktický polypropylen, Mosten 58412, byl modifikován přídavkem specifického β -nukleačního činidla založeného na *N,N'*-dicyklohexyl-2,6-naftalendikarboxamidu (NU100). Pro vysokotlakou krystalizaci bylo použito vysokotlaké krystalizační zařízení pvT100. Za různých krystalizačních tlaků a teplot byly izotermně krystalizovány čisté a nukleované směsi. Neizotermní krystalizace vzorků byla provedena pod tlakem 100 MPa při třech různých rychlostech chlazení.

Kinetika krystalizace byla studována z dilatometrických dat, širokoúhlou rentgenografií byla snímána polymorfní struktura, polarizovanou světelnou mikroskopií byla pozorována morfologická struktura, pomocí diferenciální snímací kalorimetrie byl sledován proces tání, mechanické vlastnosti reprezentované elastickým modulem a tvrdostí byly studovány dynamicko-mechanickou termální analýzou a měřením Shore D.

Acknowledgement

My great appreciate belongs to my supervisor, Martin Obadal, for his precious time, support with valuable advices and inspirational suggestions, help with experiments and language correction, that have helped me to successfully complete this master thesis.

I also appreciate to Jiřina Dohnalová for help with X-ray scattering and Jiří Maláč for DMTA measurement.

I declare, I worked on this Master thesis by myself and I have mentioned all the used literature.

Zlín, 30. May 2005

Lubomír Beníček

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INTRODUCTION

The use of polymeric materials is rapidly increasing. In many applications, they replace conventional materials such as metals, wood, and natural fibers. In today's world, a strong competition, in terms of application, between these materials exists, even among different polymeric groups. This competition is particularly based on two parameters: high end-use properties and low cost.

Isotactic polypropylene (iPP) is widely used commodity polymer with the fastest production and consumption growth. The reason is its favorable price/performance ratio and many possible applications. For example, iPP because of its good resistance to chemicals and fatigue, gained wide acceptance in applications ranging from fibers and films to injection molded parts for automobiles and food packaging. Injection molding is a widely used method for the manufacturing of a variety of these products. This technique as well as many others is conducted at elevated pressures, sometimes exceeding 200 MPa. Knowledge of the crystallization kinetics at both atmospheric and high pressure scale is thus important for determination of consequent properties.

The crystallization and processing are even more complicated by various additives. For instance, the application of various nucleating agents (nucleants) usually changes both the morphology and the polymorphic composition as well. The nucleation of polypropylene has been explored from technological and from scientific points of view. Originally, the nucleants were used as clarifying agents to modify optical properties, later it was shown that they can affect markedly also mechanical properties. The nucleation is an efficient way to control the supermolecular structure of polypropylene but at the same time the morphological changes occurs also as a function of crystallization pressure. Consequently, an understanding of the relations between pressure, nucleation and polypropylene crystallization is of considerable interest from both scientific and industrial points of view.

On the crystal lattice level, iPP exhibits three different morphological forms, α , β and γ , distinguished by the arrangement of the helical chains. Each of these forms is observed with different preparation procedures and identified with specific peaks in the X-ray pattern. The predominant crystal structure of neat iPP, at atmospheric pressure, is the monoclinic α -structure. While the most reliable method for the preparation of trigonal β -

phase is specific nucleation, the formation of orthorhombic γ -phase is particularly supported by crystallization at elevated pressures.

In this context, the aim of this work is to prove and described the crystallization technique based on synergy application of high pressure and β -nucleation during both isothermal and non-isothermal crystallization. As a consequence, this thesis provides investigation of multi-component crystalline systems in isotactic polypropylene formed by the effect of mentioned crystallization conditions. High-pressure crystallization equipment pvT100 was used for sample preparation, and dilatometric data were used for determination of crystallization kinetics. Investigation of such prepared samples was carried out using several experimental techniques, namely wide-angle X-ray scattering, polarized light microscopy, differential scanning calorimetry, dynamic-mechanical thermal analysis and hardness Shore D measurement.

I. THEORETICAL BACKGROUND

1 MORPHOLOGIES OF CRYSTALLIZED POLYMERS

The crystalline state is defined as one that diffracts X-rays and exhibits the first-order transition known as melting.

A first-order transition has normally a discontinuity in the volume-temperature dependence, as well as a heat of transition, ΔH_m , also called the enthalpy of fusion or melting. The most important second-order transition is the glass transition in which the volume-temperature dependence undergoes a change in slope, and only the derivative expansion coefficient, dv/dT , undergoes a discontinuity. There is no heat of transition at T_g , but rather a change in the heat capacity, Δc_p .

Polymers crystallized in the bulk, however, are never totally crystalline, as a consequence of their long-chain nature and subsequent entanglements. The melting (fusion) temperature of polymer, T_m , is always higher than the glass transition temperature, T_g . Thus the polymer may be either hard and rigid or flexible.

The development of crystallinity in polymers depends on the regularity of the structure in the polymer. Thus isotactic and syndiotactic polymers usually crystallize, whereas atactic polymers, with a few exceptions do not.

Nonregularity of structure first decreases the melting temperature and finally prevents crystallinity. Mers of incorrect tacticity tend to destroy crystallinity, as does copolymerization. Thus, statistical copolymers are generally amorphous. Blends of isotactic and atactic polymers show reduced crystallinity, with only the isotactic portion crystallizing [1].

The crystallization of flexible chain polymers can be carried out by supercooling of a solution or a melt in which, initially, the chain units are either randomly arranged or partially ordered. Crystallization can also occur during the polymerization process of natural or synthetically produced polymers. The crystallization process has to be started or nucleated and can be carried out quiescently or with the application of stress to the fluid. Crystallization from an isotropic polymer fluid is usually incomplete with a sizable portion remaining uncrystallized. The more common morphologies observed include [3]:

1. Faceted single lamellas containing folded or extended chains,
2. Nonfaceted lamellas,
3. Branched (dendritic) structures,
4. Sheaf-like arrays of lamellar ribbons (axialites, hedrites),
5. Spherulitic arrays of lamellar ribbons (spherulites),
6. Fibrous structures, and
7. Epitaxial lamellar overgrowths on microfibrils.

1.1 Single Lamellas

Single lamellas (platelets) can be formed by isothermal crystallization from quiescent supercooled melt or solution of a large variety of polymer with a wide range of chain flexibility.

Polymer lamellas can have a highly regular geometry, appearing to be single crystal. Lamellas with uniform size and shape can be prepared by a self-seeding technique involving simultaneous nucleation of all the lamellas and isothermal growth. Faceted lamellar geometries reported include: diamond, hexagonal, pyramidal, square and lathe shapes. Lamellas with rounded edges are also observed. The geometries observed on the type of crystal lattice adopted, the crystallization solvent and kinetic factors.

1.1.1 Chain Folding

In the crystalline part of a lamellar platelet, the polymer chains are usually oriented perpendicular, or nearly perpendicular, to the platelet faces and parallel to the edge surfaces.

A schematic representation of the center part of a polymer lamella, based on chain folding model, is shown in *Fig.I. 1*. In this drawing, each straight line represents a section of a polymer chain incorporated in the crystal lattice and contains a number of repeat units; the loops shown depict the folds. Most of the folds in this figure are tight adjacent re-entrant (region 1). A few of the folds depicted in this figure are loose adjacent re-entrant (2) and some are nonadjacent re-entrant (3); some short protruding chain ends (4) are shown.

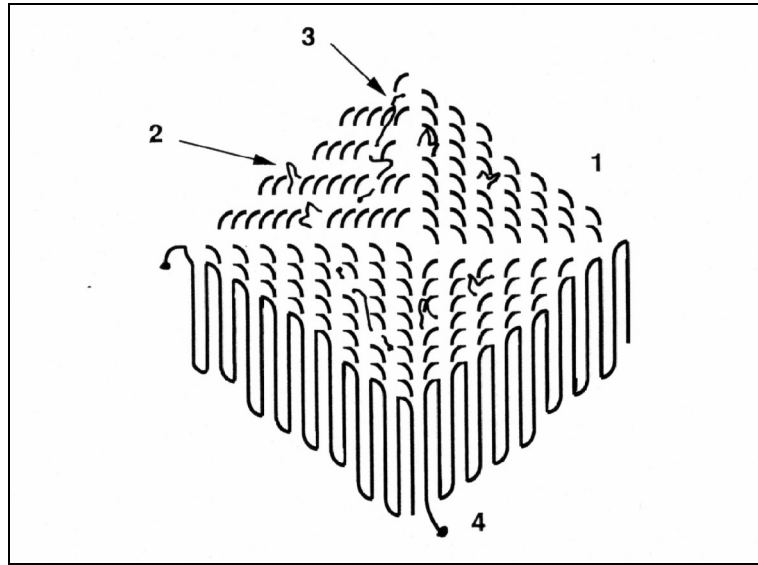


Fig.I. 1 Polymer single lamella. The numbers identify features described in text.

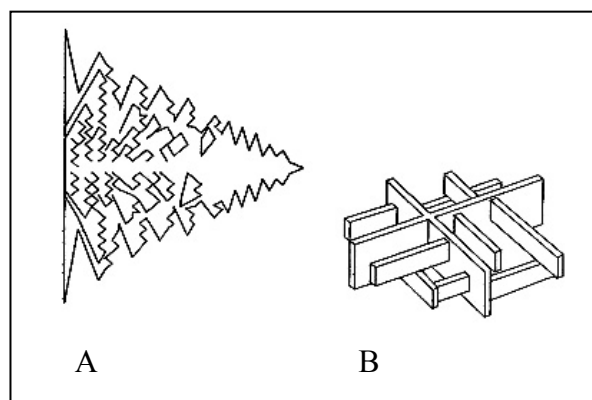
Curvature generally occur from one edge of the lamella and ridges up to 15 nm high, identified as edge-on lamellas, and is found near the curved edge.

The thickness of lamellar platelets of polymers is usually small with respect to their lateral dimensions.

One very important parameter determining the crystal stem length is the degree of supercooling, given by $T_m - T_c$, where T_m is the equilibrium melting point and T_c is the crystallization temperature. The maximum stem length possible is the length of the extended chain. Crystallization conditions leading to large stem length include high pressure, small degrees of supercooling and long crystallization time. The lamellar thickness, a parameter larger than the crystal stem length, is found experimentally to be inversely proportional to the degree of supercooling at low amounts and, then to level off at high amounts. Melting of polymer lamellas can occur at temperatures well below T_m ; the smaller the lamellar thickness, the lower the melting temperature [3].

1.2 Branched and Multilamellar Structures

Dendrites are branched lamellae with the branches related in a definite crystallographic way to each other. Branching occurs under conditions in which crystal growth from solution is fast relative to the diffusion of polymer molecules to the crystallization site. This results in lower polymer concentration at the growth faces.



*Fig.I. 2 Polymer dendrites (partial views):
A. polyethylene, B. polypropylene*

At high concentrations, thick multilayered dendrites are observed. There are various types of dendrites, two of which are shown in *Fig.I. 2*. For isotactic polypropylene interpenetrating cross-hatched dendritic structures, called quadrites, were obtained through crystallization from solution and from melt [3].

1.3 Hedrites

Hedrites (axialites) are stacks of centrally connected lamellae that grow from solution or melt [27]. The lamellae in a particular stack are probably commonly nucleated by one or more chains with elongated conformations. The lamellae are usually somewhat longer than they are wide, with growth occurring principally at the ends. During growth from solution, these lamellae can develop further connections due to the incorporation of a single chain or a group of chains in neighbouring lamellae.

When crystallization is carried out at high solution concentrations, hedrite-like structures can be obtained. Crystallization from a supercritical fluid yields hedrites. Branching, cellulation and splaying are observed in these structures. Hedrites are usually birefringent when viewed through crossed polaroids [3].

1.4 Spherulites

When polymer samples are crystallized from the melt, spherulites are the most obvious observed structures. As the name implies, spherulites are sphereshaped crystalline structures that form in the bulk. One of the more important problems to be addressed concerns the form of the lamellae within the spherulite. Spherulites are remarkably easy to grow and observe in the laboratory. Simple cooling of a thin section between crossed polarizers is sufficient, although controlled experiments are obviously more demanding. It is observed that each spherulite exhibits an extinction cross, sometimes called a Maltese cross. This extinction is centered at the origin of the spherulite, and the arms of the cross are oriented parallel to the vibration directions of the microscope polarizer and analyzer.

Usually the spherulites are really spherical in shape only during the initial stages of crystallization. During the latter stages of crystallization, the spherulites impinge on their neighbors. When the spherulites are nucleated simultaneously, the boundaries between them are straight. However, when the spherulites have been nucleated at different times, so that they are different in size when impinging on one another, their boundaries form hyperbolas. Finally, the spherulites form structures that pervade the entire mass of the material.

A model of the spherulite structure is illustrated in *Fig.I. 3*. The chain direction in the bulk-crystallized lamellae is perpendicular to the broad plane of the structure, just like the dilute solution crystallized material.

The spherulite lamellae also contain low-angle branch points, where new lamellar structures are initiated. New lamellae tend to keep spacing between the crystallites constant.

While the lamellar structures in the spherulites are the analogue of the single crystals, the folding of the chains is much more irregular. In between the lamellar structures lies amorphous material. This portion is rich in components such as atactic polymers, low-molecular-weight material, or impurities of various kinds.

The individual lamellae in the spherulites are bonded together by tie molecules, which lie partly in one crystallite and partly in another. Sometimes these tie molecules are actually in the form of what are called intercrystalline links, which are long, threadlike crystalline structures with the *c* axis along their long dimensions. These intercrystalline

links are thought to be important in the development of the great toughness characteristic of semicrystalline polymers. They serve to tie the entire structure together by crystalline regions and/or primary chain bonds [1].

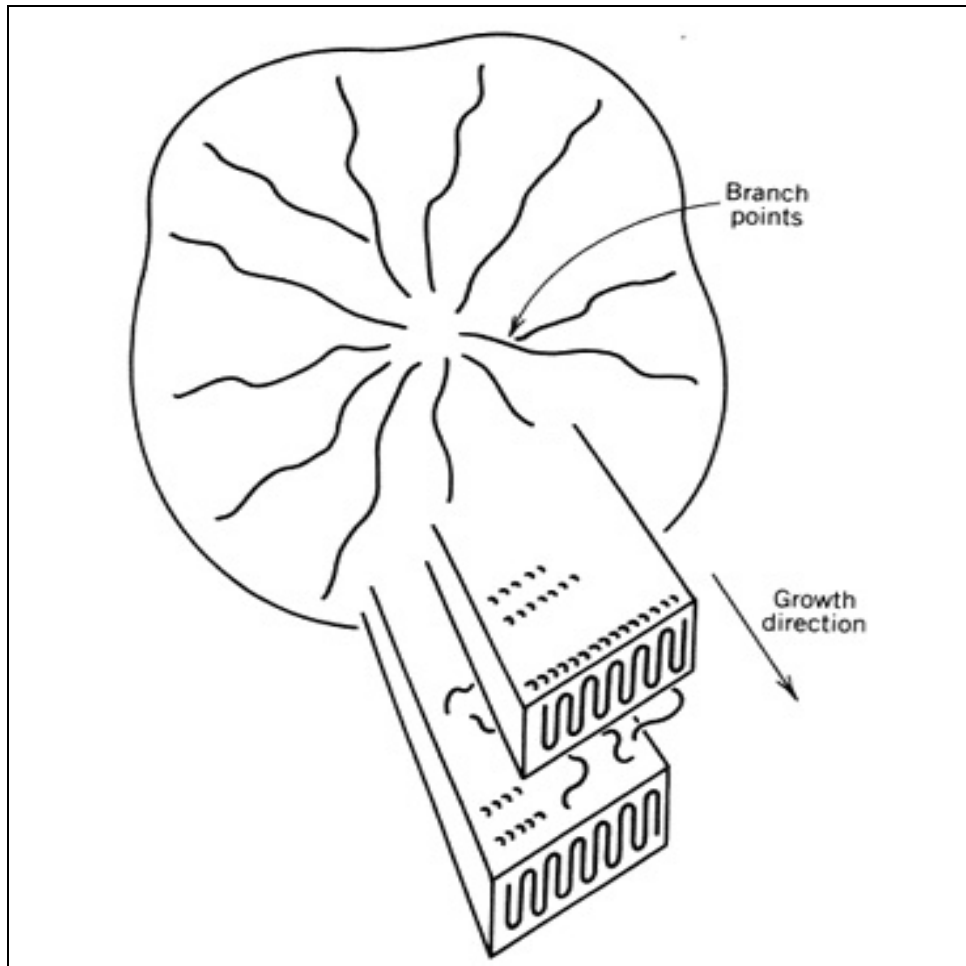


Fig.I. 3 Model of spherulitic structure. Note the growth directions and lamellar branch points that fill the space uniformly with crystalline material [29]

1.4.1 Mechanism of Spherulite Formation

On cooling from the melt, the first structure that forms is the single crystal. These rapidly degenerate into sheaflike structures during the early stages of the growth of polymer spherulites (see *Fig.I. 3*). These sheaflike structures have been variously called axialites or hedrites. These transitional, multilayered structures represent an intermediate stage in the formation of spherulites. It is evident that as growth proceeds, the lamellae develop on either side of a central reference plane. The lamellae fan out progressively and grow away from the plane as the structure begins to mature.

The sheaflike structures are modeled in *Fig.I. 4*. Gradually the lamellae in the hedrites diverge or fan outward in a splaying motion. Repeated splaying perhaps aided by lamellae that are intrinsically curved and eventually leads to the spherical shape characteristic of the spherulite [1].

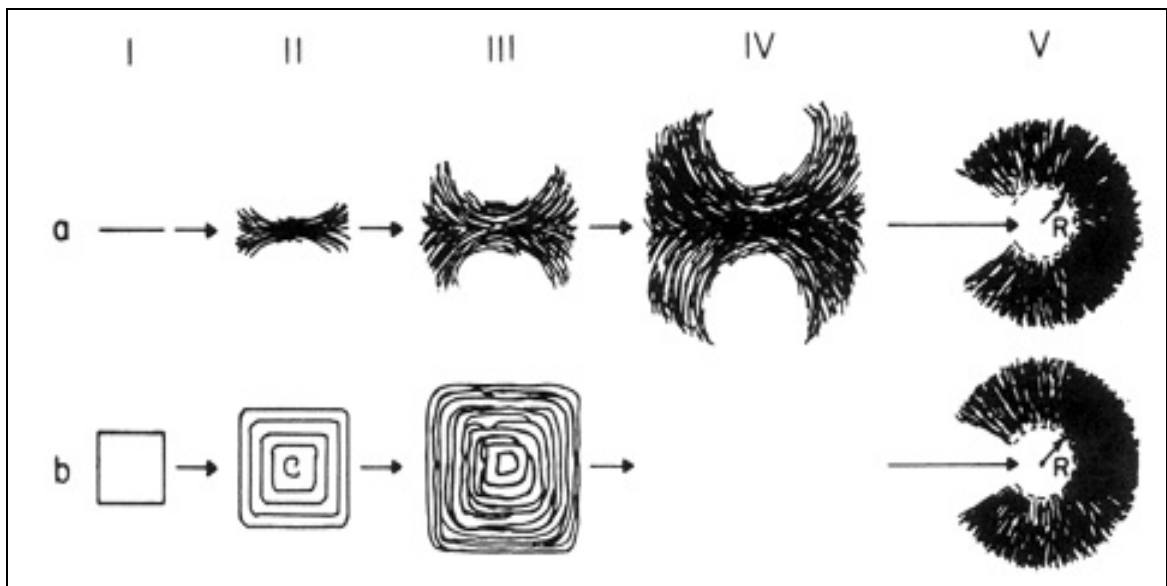


Fig.I. 4 Schematic development of a spherulite from a chain-folded precursor crystal. Rows (a) and (b) represent, respectively, edge-on and flat-on views of the evolution of the spherulite.

2 KINETICS OF CRYSTALLIZATION

During crystallization from the bulk, polymers form lamellae, which in turn are organized into spherulites or their predecessor structure, hedrites. This section is concerned with the rates of crystallization under various conditions of temperature, molecular weight, structure, and so on, and the theories that provide not only an insight into the molecular mechanism but considerable predictive power [1].

The thermodynamic description of the crystallization process, can be written

$$\Delta G = G_{crystal} - G_{melt} \quad (1)$$

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

where ΔG is the free enthalpy (Gibbs free energy) of the crystallization and ΔH and ΔS are the enthalpy and entropy of crystallization. Equation (2) applies to the overall macroscopic transformation. Crystallization becomes possible as soon as ΔG assumes negative values. If the phase transition would strictly follow Eq. (2), crystals grown on cooling would have to be distributed uniformly over the volume, which has reached the melting temperature T_m at which ΔG is zero. Polymer melts and solutions T_c , they supercool. In addition, crystals grow from a nucleus rather than generate uniformly throughout the random phase.

The reason for supercooling and the need for nucleation can be found by analyzing the crystallization process in more detail [2].

Theories of Crystallization Kinetics

Keller's preparations of single crystal from dilute solutions, since the crystals were only about 100Å thick and the chains were oriented perpendicular to the flat faces, Keller postulated that the chains had to be folded back and forth.

Similar structures, called lamellae, exist in the bulk state. While their folding is now thought to be much less regular, their proposed molecular organization remains similar. In the bulk state, however, these crystals are organized into the larger structures known as spherulites. The rate of radial growth of the spherulites is linear in time and the rate of growth goes through a maximum as the temperature of crystallization is lowered. These several experimental findings form the basis for three theories of polymer crystallization kinetics.

The first of these theories is based on the work of Avrami, which adapts formulation intended for metallurgy to the needs of polymer science. Keith and Padden, providing a qualitative understanding of the rates of spherulitic growth, developed the second theory. More recently, Hoffman and co-workers developed the kinetic nucleation theory of chain folding, which provides an understanding of how lamellar structures form from the melt. This theory continues to be developed [1].

2.1 The Avrami Equation

The original derivations by Avrami have been simplified by Evans and put into polymer context by Maeres and Hay. In the following, it is helpful to imagine raindrops falling in a puddle. These drops produce expanding circles of waves that intersect and cover the whole surface. The drops may fall sporadically or all at once. In either case they must strike the puddle surface at random points. The expanding circles of waves, of course, are the growth fronts of the spherulites, and the points of impact are the crystallite nuclei.

X_t is the volume fraction of crystalline material, known widely as the degree of crystallinity.

The familiar form of the Avrami equation:

$$1 - X_t = e^{-Zt^n} \quad (3)$$

which is often written in the logarithmic form:

$$\ln(1 - X_t) = -Zt^n \quad (4)$$

K replaces the quantity Z in some books,

Both Z and n are diagnostic of the crystallization mechanism. The equation has been derived for spheres, discs, and rods, representing three-, two-, and one-dimensional forms of growth. The constants are summarized in *Tab.I. 1*.

The Avrami equation represents only the initial portions of polymer crystallization correctly. The spherulites grow outward with a constant radial growth rate until their impingement takes place when they stop growth at the intersection.

Then a secondary crystallization process is often observed after the initial spherulite growth in the amorphous interstices [1].

Tab.I. 1 The Avrami parameters for crystallization of polymers

	Crystallization Mechanism	Avrami Constants		Restrictions
		Z	n	
Spheres	Sporadic	$2/3\pi g^3 l$	4.0	3 dimensions
	Predetermined	$4/3\pi g^3 L$	3.0	3 dimensions
Discs ^a	Sporadic	$\pi/3g^2 ld$	3.0	2 dimensions
	Predetermined	$\pi g^3 Ld$	2.0	2 dimensions
Robs ^b	Sporadic	$\pi/4gld^2$	2.0	1 dimension
	Predetermined	$1/2\pi gLd^2$	1.0	1 dimension

^aconstant thickness d, ^bconstant radius d, sporadic = homogenous, predetermined = heterogenous

According to ref. [2], the exponent n may show values ranging from below 1 to far above 6. Any one value, whole or fractional, however, is not uniquely fixed to any one set of conditions. Additional information on nucleation, morphology, and possibly even mechanism is necessary to fully interpret the exponent n . Special caution is necessary due to the strong correlation between K , t , and n , which may hide changes in n by correlated changes in K and t_0 .

2.2 Keith-Padden Kinetics of Spherulitic Crystallization

Although the Avrami equation provides useful data on the overall kinetics of crystallization, it provides little insight as to the molecular organization of the crystalline regions, structure of the spherulites, etc.

Section 1.4 describes the phenomenon - how the spherulites are composed of lamellar structures that grow outward radially. The individual chains are folded back and forth tangentially to the growing spherical surface of the spherulite (see Fig.I. 5). Normally, the rate of growth in the radial direction is constant until the spherulites meet. As the spherulites grow, the individual lamellae branch. Impurities, atactic components, etc., become trapped in the lamellar regions [1].

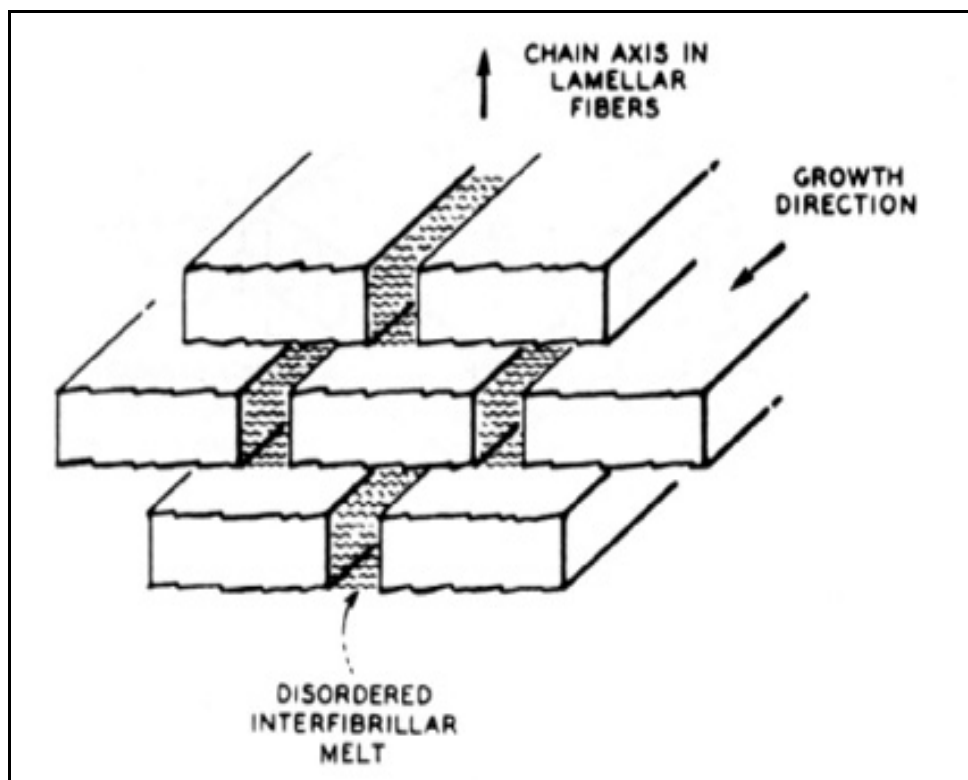


Fig.I. 5 Schematic representation of the distribution of residual melt and disordered material among lamellae in a spherulite

2.3 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 mechanism, particularly the thermodynamics and kinetics of the phenomenon.

More recently, Hoffman and co-workers attacked the kinetics of polymer crystallization anew. Hoffman began with the assumption that chain folding and lamellar formation are kinetically controlled, the resulting crystals being metastable. The thermodynamically stable form is the extended crystal, obtained by crystallizing under pressure.

The basic model is illustrated in *Fig.I. 6* where l is the thin dimension of the crystal, x the large dimension, σ_e the fold surface interfacial free energy, and σ the lateral surface interfacial free energy, a single chain making up the entire crystal [1].

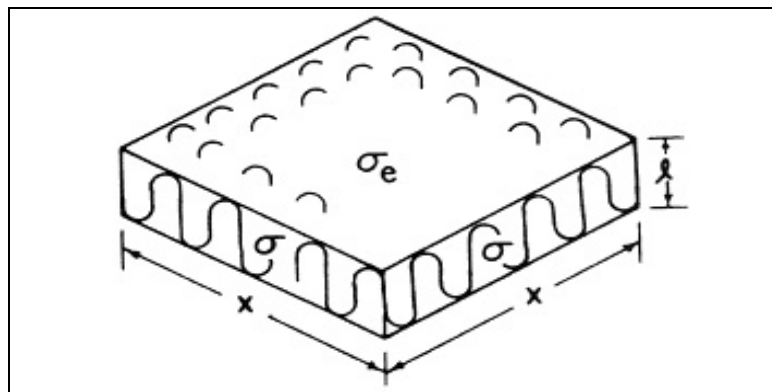


Fig.I. 6 Thin chain-folded crystal showing σ and σ_e (schematic)
[29]

3 POLYPROPYLENE

Polypropylene is a versatile thermoplastic material, compatible with many processing techniques and used in many different commercial applications. It is one of the fastest growing classes of commodity thermoplastic. The moderate cost and favorable properties of polypropylene contribute to its strong growth rate [4].

3.1 Polymerization

In 1954 Giulio Natta following the work of Karl Ziegler found that certain ‘Ziegler-type’ catalysts were capable of producing high molecular weight polymers from propylene and many other olefins. By variations on the form of the catalysts used, Natta was able to produce a number of different types of high molecular weight polypropylenes which differed extensively in their properties. One form, now known as isotactic polypropylene, was in many ways similar to high-density polyethylene but with a higher softening point, rigidity and hardness, whilst another form, the atactic polymer, was amorphous with low strength.

The monomer for PP production is obtained by the cracking of petroleum products, such as natural gas or light oils. For the preparation of polypropylene the C₃ fraction (propylene and propane) is the basic intermediate and it can be separated from the other gases without undue difficulty by fractional distillation. Polypropylene is then prepared using Ziegler-type catalysts or metallocene catalysts by a polymerization. A typical catalyst system may be prepared by reacting titanium trichloride with aluminium triethyl, aluminium tributyl or aluminium diethyl monochloride in naphtha under nitrogen to form slurry consisting of about 10% catalyst and 90% naphtha. The properties of the polymer are strongly dependent on the catalyst composition and its particle shape and size [5].

3.2 Stereospecificity

With Ziegler-Natta or metallocene catalysts, the polymerization reaction is highly stereospecific. Propylene molecules add to the polymer chain only in a particular orientation, depending on the chemical and crystal structure of the catalyst, and a regular, repeating three-dimensional structure is produced in the polymer chain. Propylene molecules are added to the main polymer chain, increasing the chain length, and not to one of the methyl groups attached to alternating carbon atoms (the pendant methyl groups),

which would result in branching. Propylene molecules are usually added head-to-tail and not tail-to-tail or head-to-head. Head-to-tail addition results in a polypropylene chain with pendant methyl groups attached to alternating carbons; in tail-to-tail or head-to-head addition, this alternating arrangement is disrupted. Occasional tail-to-tail or head-to-tail additions of polypropylene to the growing polymer chain disrupt the crystalline structure and lower the melting point of the polymer; formulations in which this occurs are used in thermoforming or blow molding.

Polypropylene can be isotactic, syndiotactic, or atactic, depending on the orientation of the pendant methyl groups attached to alternate carbon atoms. In isotactic polypropylene (*Fig. I. 7*), the most common commercial form, pendant methyl groups are all in the same configuration and are on the same side of the polymer chain. Due to this regular, repeating arrangement, isotactic polypropylene has a high degree of crystallinity. In syndiotactic polypropylene, alternate pendant methyl groups are on opposite sides of the polymer backbone, with exactly opposite configurations relative to the polymer chain. Syndiotactic polypropylene is now being produced commercially using metallocene catalysts. In atactic polypropylene, pendant methyl groups have a random orientation with respect to the polymer backbone. The used catalyst and the polymerization conditions determine amounts of isotactic, atactic, and syndiotactic segments in a formulation. Most polymers are predominantly isotactic, with small amounts of atactic polymer. New metallocene catalysts make possible other stereochemical configurations, such as hemi-isotactic polypropylene. In this configuration, the most pendants methyl groups are on the same side of the polypropylene chain, as in isotactic polypropylene; however, other methyl groups are inserted at regular intervals on the opposite side of the chain [4].

These stereo-isomeric configurations also induce stable, specific overall conformations of the polymer chain: helix $2_1 \times 3_1$ for the isotactic PP, helix $4_1 \times 2_1$ for the syndiotactic PP and a random conformation for atactic PP. The stable regular conformations of isotactic and syndiotactic chains promote crystallization by parallel organization of chain segments issued from the same chain or from chains in the vicinity [7].

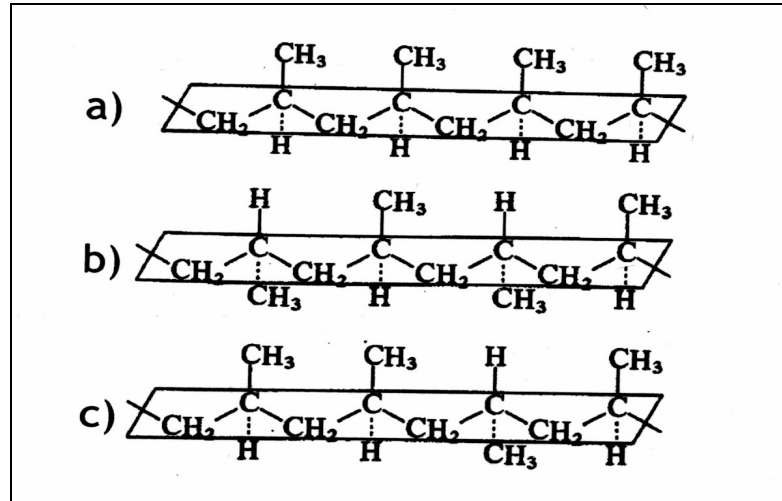


Fig.I. 7 Stereo-configurations of propylene sequences:
 a) isotactic; b) syndiotactic; c) atactic [6]

3.3 Properties of PP

Mechanical properties of PP strongly depend on its crystallinity. Increasing crystallinity enhances stiffness, yield stress, and flexural strength, however, decreases toughness and impact strength [4].

PP indicates some similar properties to polyethylene (PE), particularly swelling and solution behavior, and electrical properties. In spite of the many similarities the presence of a methyl group attached to alternate carbon atoms on the chain backbone alters the properties of the polymer in a number of ways. For example, the tertiary carbon atom provides a site for oxidation so that the polymer is less stable than PE to the influence of oxygen [4].

Comparison of properties of all stereo-isomers of polypropylene is given in *Tab.I. 2* [6].

Tab.I. 2 Properties of isotactic, syndiotactic and atactic PP

Property	Isotactic PP	Syndiotactic PP	Atactic PP
Density (kg.m ⁻³)	920 - 940	800 - 910	850 - 900
Melting temperature (°C)	165	135	-
Solubility in hydrocarbons (20°C)	no	middle	high
Yield strength	high	middle	very low

3.4 Polymorphism in Isotactic Polypropylene

Polypropylene can exist in different morphological forms, depending on the tacticity of the material and the crystallization conditions, such as pressure, temperature, and cooling rate. Different forms can coexist, and one polymorphic form can change into another as conditions change [4].

Three crystalline forms are known for isotactic PP: monoclinic α -phase, trigonal β -phase and orthorhombic γ -phase [7]. Each of these forms is observed with different preparation procedures and identified with specific peaks in the X-ray pattern as shown in *Fig.I. 8* [25].

The crystallographic data of isotactic polypropylene are in *Tab.I. 3* [1].

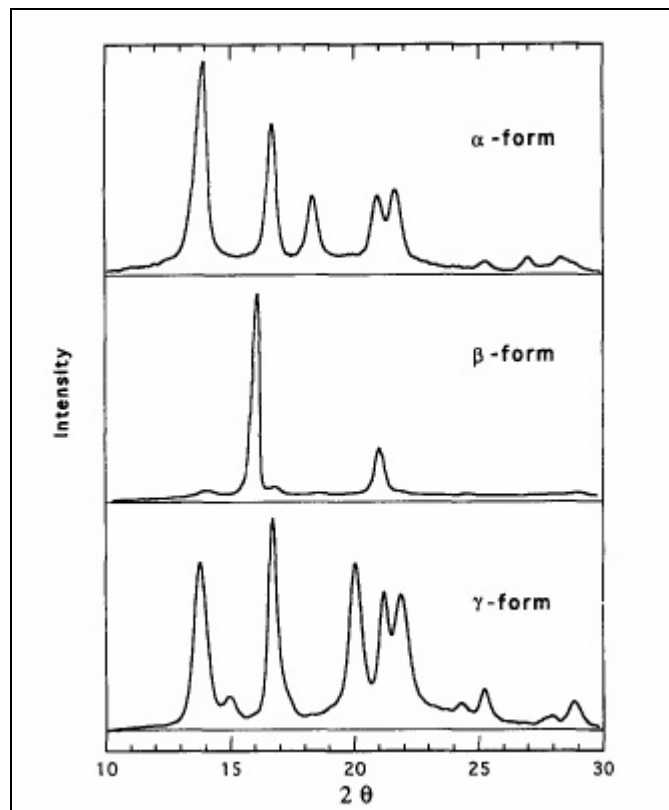


Fig.I. 8 WAXS of different morphological forms of isotactic polypropylene

Tab.I. 3 Crystallographic data of iPP

Crystal System, Space Group, Lattice Constants, and Number of Chains per Unit Cell	Molecular Conformation	Crystal Density (g/cm ³)
α -phase, monoclinic, C2/c-C _{2h} ⁶ of Cc-C _s ⁴ , a=6.65Å, b=20.96Å, c=6.50Å, β =99°20'. N=4	Helix (3/1) (TG) ₃	0.936
β -phase, trigonal, a=19.08Å, c=6.49Å, N=9	Helix (3/1) (TG) ₃	0.922
γ -phase, orthorhombic, P3 ₁ 21-D ₃ ⁴ or P3 ₂ 21-D ₃ ⁶ , a=6.38Å, c=6.33Å, N=6	Helix (3/1) (TG) ₃	0.939

3.4.1 α - phase

The crystal structure of the most common crystal phase of iPP – the α -phase – as established by Natta and Corradini is reproduced in *Fig.I. 9* [8]

Polymer chains in the α -phase form a helical structure in a monoclinic unit cell, and fold into lamellae with thicknesses of 50– 200 Å. Radial growth of lamellae is dominant; however, lamellae can also associate tangentially, with the tangential lamella branching off approximately orthogonally from the plane of the radial lamellae. This forms a cross-hatched structure in the lamellae, which aggregate to form spherulites. The lamellar structure produces positive, negative, and mixed birefringence. Negative birefringence results from spherulites in which radial lamella are dominant, while positive birefringence is due to spherulites with predominantly tangential lamellae. Both negatively and positively birefringent spherulites form a Maltese cross pattern under crossed polarizers. In spherulites with mixed birefringence, neither tangential nor radial lamellae are predominant, and a distinct Maltese cross is not formed. The birefringence changes from positive to negative with increasing crystallization temperature, as the tangential lamellae undergo premelting. The α -phase of isotactic polypropylene is the primary phase of polypropylene obtained under usual processing conditions [4].

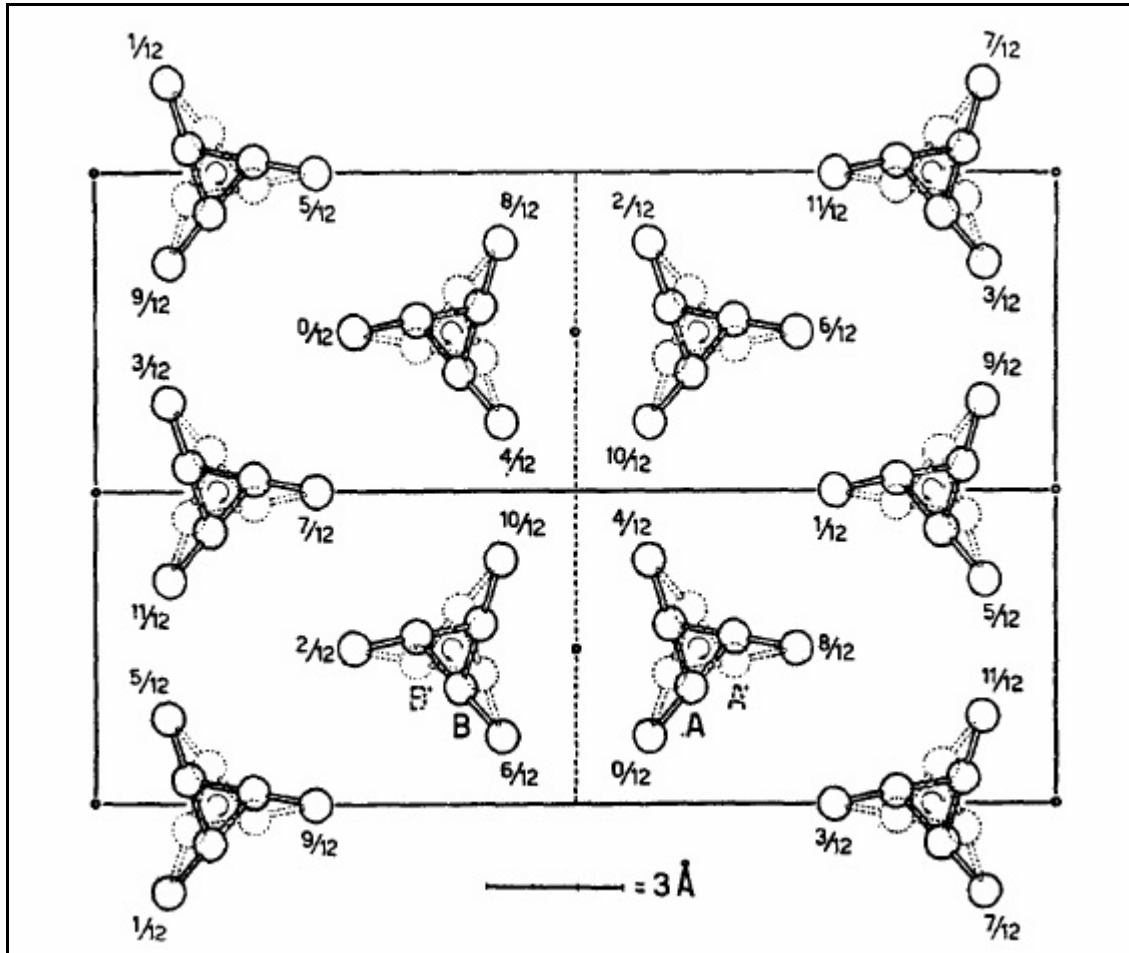


Fig.I. 9 Crystal structure of α -phase of iPP as determined by Natta and Corradini. Two unit cells are shown. a^* axis vertical, b axis horizontal. The crystal structure includes statistical occupation of every chain site by either an up- or a down-pointing chain

3.4.2 β - phase

The β -phase has a trigonal unit cell structure, with more disorder than the α -phase (see Fig.I. 10). The parallel, stacked lamella does not show cross-hatching. Lamella have been observed to form sheaf-like spherulitic structures with interconnected boundaries, different from the distinct boundaries of α -phase spherulites; in experiments with high purity β -phase polypropylene, this structure resulted in lower elastic module and yield strength at a given strain rate and higher impact strength and breaking strain values than α -phase polypropylene [11],[12]. The β -phase exhibits negative birefringence under crossed polarizers and can convert to the α -phase on heating. Polypropylene can crystallize in the β -phase at relatively low isothermal crystallization temperatures or in the presence of various nucleating agents, [4].

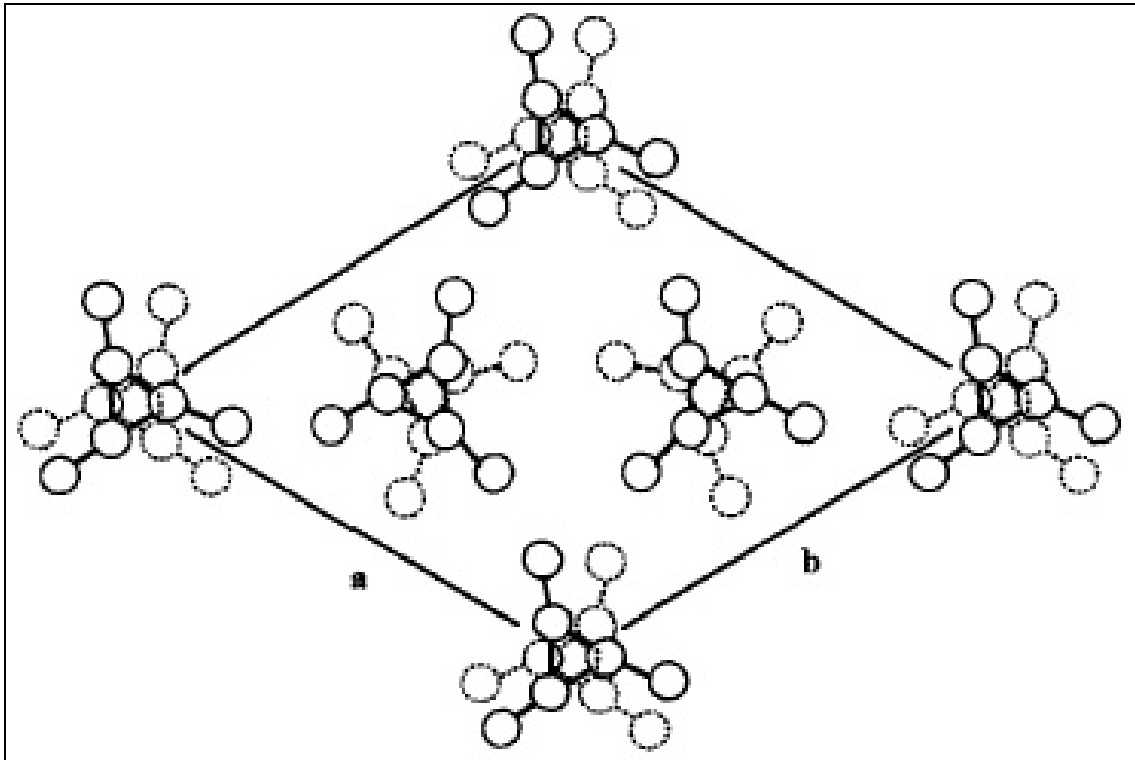


Fig.I. 10 Unit cell and structure of β -phase of iPP [8]

In comparison with α -iPP, β -iPP has a lower elastic modulus and yield stress, but higher ultimate tensile strength and strain. The improvement in the latter might be related to the $\beta\alpha$ -transition occurring during the necking, which leads to the formation of α -modification of enhanced strength (strain-hardening). The impact strength and toughness of β -iPP exceed those of α -iPP. The improvement in toughness and impact strength could be attributed to β to α or (at low deformation rate) to β to smectic transition occurring during the deformation [14]. Another possible reason for superior toughness could be connected to the peculiar morphology of β -iPP [15] and its continuity with amorphous phase [16].

According to DMTA (Dynamic Mechanical Analysis) measurements the intensity of glass transition (T_g), i.e. the value of the loss modulus at T_g , and the storage modulus below T_g , increase with the β -content of samples showing mixed polymorphic composition. These findings suggest that β -iPP possesses a lower crystallinity than α -iPP, which contributes to a toughness increase for β -iPP. Nevertheless, direct measurements on the crystallinity contradicted the above assumption, i.e. the crystallinity increases with increasing β -content [9]. Similar effect was observed also by differential scanning calorimetry [11]. The explanation for this discrepancy is supposed that the coupling

between the crystalline and amorphous phase in β -iPP is weaker than that in α -iPP. This assumption seems to be confirmed by considering the superior damping behavior of β -iPP under impact loading (i.e. the missing load oscillation in the fractograms of β -iPP). In spite of the lower melting temperature of β -iPP, its heat distortion temperature exceeds that of α -iPP. This could be explained by the $\beta\alpha$ -recrystallization during heating, which generates a α -modification of higher melting temperature [9].

3.4.3 γ - phase

The γ -phase of isotactic polypropylene was initially considered to have a triclinic unit cell with dimensions similar to the α -phase, but the crystal structure was recently reassigned as an orthorhombic unit cell with nonparallel, crossed lamellae. *Fig.I. 12* shows four unit cells of the γ -modification formed by 3_1 -helices of iPP. Calculations of the packing energies of the γ - and α - modifications show that the γ -modification should be slightly more stable than the α -modifications [17].

It should be mentioned that the supermolecular morphologies formed by the γ -phase are very different from the typical spherulitic structures of α - or β - phase iPP. Real spherulites are formed in samples where the α - and γ - modifications appear simultaneously and the amount of the α -modification exceeds 30%. It is also possible to prepare single crystals of the γ -modification iPP. In addition, in this case an ongrowth of γ -phase iPP on α -phase lathes can be observed. Single crystal of the neat γ -phase have a triangular appearance [18].

In experiments with polypropylene crystallized at high pressures and different crystallization temperatures, the crossed lamellae formed a feather-like structure (*Fig.I. 11*) that was shown from microscopy to result from self-epitaxial (tangential) growth. γ -form polypropylene does not usually form under typical processing conditions. It can occur in low molecular weight materials ($M_n \sim 6000$), during crystallization at elevated pressures, or in chains with regular defects, produced using metallocene catalysts. The α -form is present at atmospheric pressure; as the pressure is increased, the γ -form begins to coexist with the α -form until it becomes dominant at a pressure of 200 MPa [4].



Fig.I. 11 Reflection optical micrograph of lamellae in isotactic polypropylene arranged in feather-like structures. The polypropylene sample was crystallized isothermally at 203°C and 200 MPa and was permanganically etched for 30 minutes.

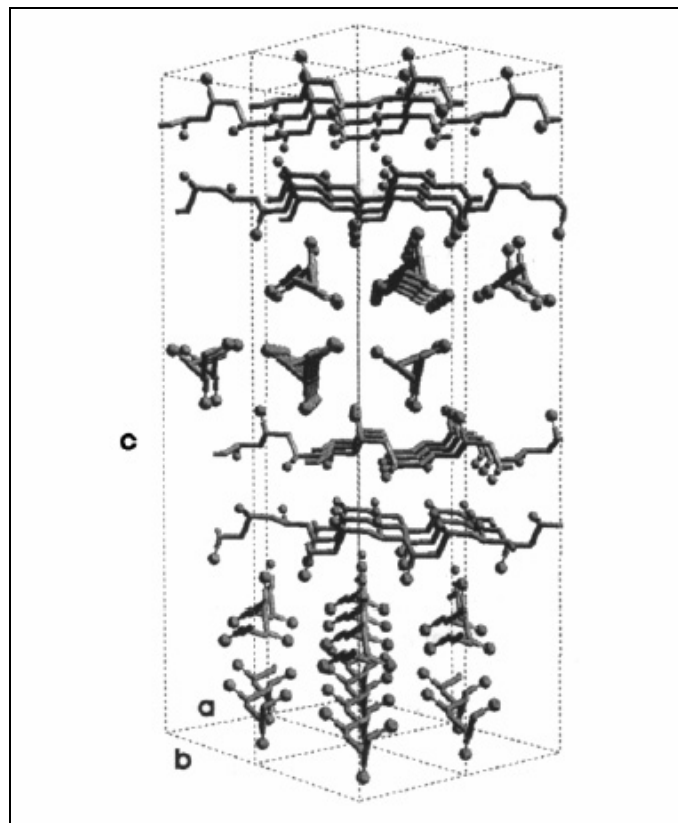


Fig.I. 12 Four unit cells of the γ -modification of iPP according to the nonparallel chain packing model of Meille et. al. [17]. The spherical entities represent the methyl groups.

3.4.4 Smectic form

The mesomorphic or smectic form of polypropylene is a noncrystalline phase, intermediate in order between crystalline and amorphous forms. Early experiments indicated that this form might be a paracrystalline phase resulting from deformed or distorted lattice structures. Examples of lattice defects include atoms forced out of normal lattice or unit cell positions due to surrounding amorphous material, changes in polymer chain folding, the presence of atoms of foreign material in the lattice, and screw dislocations that disrupt the spherulite structure by initiating lamellar growth in an irregular location. Polymer chains have been shown to form helical structures, but the unit cell and lamellar structures have not yet been well resolved. Experiments indicate a lack of lamellar order in addition to a low density and small size of ordered structures. These characteristics result in high clarity, useful in quenched film applications [4].

3.5 Nucleating agents

Nucleating agents are purposefully added to polypropylene to improve processing characteristics and clarity, and to alter its mechanical properties. The addition of nucleating agents provides a large number of sites for the initiation of crystallization, so that spherulites formed are smaller and more numerous than in unnucleated polypropylene. Nucleation increases the crystallization temperature and the rate of crystallization; as a result, parts can be removed from the mold at higher temperatures, and molding cycle times are reduced. Crystallization is more complete in nucleated material than in unnucleated material, producing high levels of crystallinity. Nucleated materials have higher tensile strength, stiffness, flexural module and heat deflection temperatures than unnucleated materials, but impact strength is lower. The high levels of crystallinity can result in reduced tolerance to radiation sterilization as compared to unnucleated polypropylene, and the effectiveness of hindered amine light stabilizers and other stabilizing additives can be reduced. Because nucleated polypropylene shrinks more rapidly in the mold, shrinkage of the resin onto mold cores can occur if parts are not ejected fast enough. Clarity is enhanced due to the increased cooling rate and the decreased spherulite size, which reduces the scattering of light as it passes through the material. Smaller spherulites can reduce warpage in some applications and can provide a harder, more stainresistant surface. Nucleating agents used in polypropylene include carboxylic acid salts, benzyl sorbitols, and salts of organic phosphates. Carboxylic acid salts provide limited clarity enhancement but do enhance the mechanical properties by an increase in the crystallization rate. Dibenzylidene sorbitols reduce crystal size dramatically, resulting in greatly improved clarity. Benzyl sorbitols can result in odor generation during processing which produces odor in the finished part. Pigments, such as phthaloxyanine blue and green and phthalyl blue, and mineral fillers such as talc can also act as nucleating agents, although talc is not taken as effective. Applications of nucleated polypropylene include food bottles and packaging, automobile parts, medical syringes, and houseware containers [4].

It is worth noting that the nucleation is often specific, resulting in the growth preference of a given crystalline structure during polypropylene crystallization.

4 METHODS OF ANALYSIS

4.1 Methods for Determination of Crystal Structure

There are four basic methods in wide use for the study of polymer crystallinity: X-ray diffraction, electron diffraction, infrared absorption, and Raman spectra. The first two methods constitute the fundamental basis from crystal cell size and form, and the latter two methods provide a wealth of supporting data such as bond distances and intermolecular attractive forces [10].

4.1.1 X-Ray Methods

By considering crystals as reflecting gratings for X-rays, Bragg derived his now famous equation for the distance d between successive identical planes of atoms in the crystal:

$$d = \frac{n\lambda}{2\sin\theta} \quad (5)$$

where λ is the X-ray wavelength, θ is the angle between the X-ray beam and these atomic planes, and n represents the order of diffraction, a whole number. It turns out that both the X-ray wavelength and the distance between crystals produces a series of spots. See *Fig.I. 13*.

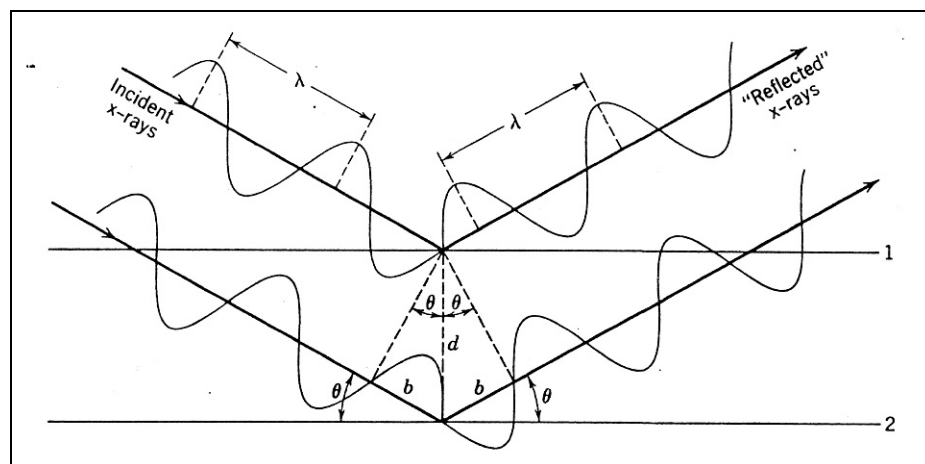


Fig.I. 13 Geometry of the Bragg reflection analogy [28]

However, not every crystalline substance can be obtained in the form of macroscopic crystals. This led to the Debye-Scherrer method of analysis for powdered crystalline solids or polycrystalline specimens. The crystals are oriented at random so the spots become cones of diffracted beams that can be recorded either as circles on a flat photographic plate or as arcs on a strip of film encircling the specimen. The latter method permits the study of back reflections as well as forward reflections.

Basically, the intensity of the diffraction spot or line depends on the scattering power of the individual atoms, which in turn depends on the number of the atoms with regard to the crystal planes, the angle of reflection, the number of crystallographically equivalent sets of planes contributing, and the amplitude of the thermal vibrations of the atoms. Both the intensities of the spots or arcs and their positions are required to calculate the crystal lattice [10].

4.1.1.1 Percent Crystallinity in Polymers

Most polymers are semicrystalline; that is, a certain fraction of the material is amorphous, while the remainder is crystalline. The reason why polymers fail to attain 100% crystallinity is kinetic, resulting from the inability of the polymer chains to completely disentangle and line up properly in a finite period of cooling or annealing.

There are several methods for determining the percent crystallinity in such polymers. The first involves the determination of the heat of fusion of whole sample by calorimetric methods such as DSC.

A second method involves the determination of the density portion via X-ray analysis of the crystal structure, and determining the theoretical density of a 100% crystalline material. The density of the amorphous material can be determined from an extrapolation of the density from the melt to the temperature of interest.

A third method stems from the fact that the intensity of X-ray diffraction depends on the number of electrons involved and is thus proportional to the density. Besides Bragg diffraction lines for the crystalline portion, there is an amorphous halo caused by the amorphous portion of the polymer. This last occurs at a slightly smaller angle than the corresponding crystalline peak, because the atomic spacings are larger. The amorphous halo is broader than the corresponding crystalline peak, because of the molecular disorder.

This third method, sometimes called wide-angle X-ray scattering (WAXS), can be quantified by the crystallinity index, CI ,

$$CI = \frac{A_c}{A_a + A_c} \quad (6)$$

where A_c and A_a represent the area under the Bragg diffraction line and corresponding amorphous halo, respectively.

Naturally, these methods will not yield the same answer a given sample, but surprisingly good agreement is obtained. For many semicrystalline polymers, the crystallinity is in the range of 40% to 75%. Of course, annealing usually increase crystallinity, as does orientation the polymer in fiber or film formation [10].

4.1.2 Polarized Light Microscopy

This simple technique only requires a polarizing filter below the condenser (the polarizer) and a second filter (the analyzer) above the specimen. Polarized microscopy is also useful for studying the thoroughness of mixing, various defects and inclusions in semicrystalline polymers.

The thickness of samples for polarized microscopy is largely depended on the polymer being analyzed. For instance, in case of polypropylene or poly(butylenes terephthalate) the spherulitic structures are very fine and therefore sections with thickness of several microns are required.

Samples can be viewed between cross polars, using a polarized optical microscope to determine if the polymer is crystalline or has in-built orientation. If there is no specimen between the cross polar, then the field of view should be completely dark. By inserting a crystalline or oriented sample between the polars, the plane of polarized light is rotated and the sample appears bright. In white light, some colors are transmitted and others are not, and because of this birefringence, the sample appears brightly colored.

Very useful information can be obtained by interpreting the birefringence observed when a crystalline or oriented sample is viewed between cross polars. Polymer melts or stress-free glassy polymers show no optical anisotropy, and therefore the field of view is black. The main use of polarized microscopy has been to study the spherulitic morphology of semicrystalline polymers.

Under polarized light, semicrystalline polymers generally show banded polyhedral spherulites that impinge upon one another. The spherulites have sharp boundaries and a dark Maltese-cross (or isogyral extinction pattern) which is characteristic of spherulitic structures. The twisting nature of the radiating spherulitic fibrils produces regions in which the molecular axis is parallel to the direction of the polarized illumination. These areas of zero birefringence are seen as concentric extinction rings.

The degree of orientation at different regions of the image can be estimated by using a tint plate (or lambda plate), which is a compensator inserted at a 45° angle between the polarized filters. This causes blue or yellow interference colors to be observed [10].

4.2 Thermal Analysis of Polymers

There are varieties of thermoanalytical techniques available in polymer science, but the most commonly used technique is differential scanning calorimetry (DSC). Other common techniques and their applicability to polymer systems are dynamic mechanical thermal analysis (DMTA), thermomechanical analysis (TMA) and thermogravimetry (TG). DSC measures the exothermic and endothermic responses of the polymer as it is heated through thermal transitions. DMTA enables the analyst to link phase transition of the polymer with its mechanical properties. There is a correlation between loss processes and toughness, vibration damping, frictional characteristics, etc. TG measures the weight change of the sample as a function of temperature, while TMA, measures the dimensional changes of the sample due to temperature effects. *Tab.I. 4* lists these common thermal analysis techniques and their practical application to polymers [10].

Tab.I. 4 Thermal analysis techniques and examples of their practical application

THERMAL ANALYSIS METHODS	
DSC	melting temperature glass transition temperature degree and rate of crystallization degree of cure
TG	thermal stability volatility of additives filler content moisture content blend composition
DMTA	creep effects stress relaxation effects damping properties vibration damping molecular transition other than T_g
TMA	degree of linear expansion/contraction with temperature delamination temperature degree of polymer hardness with temperature glass transition temperature
DETA	dielectric loss factor molecular transition due to polar groups

4.2.1 Differential Scanning Calorimetry

DSC is the most often used by polymer analysts for determining a polymer's melting temperature, glass transition temperature, degree of crystallinity, heat of fusion or degree of cure, etc.

Although DSC has become a routine method for polymer analysis, the analyst needs to be aware of possible artifacts that can distort the results. Careful interpretation of thermoanalytical data can provide a wealth of information for polymer characterization. It is well known that the first heating curve is significantly influenced by the sample's thermal history. It is often useful therefore to compare the first and second heating scan of a polymer sample. Information that can be obtained by this comparison can be related to the thermal history (mold temperature, etc.), crystallinity and recrystallization. It should be noted that, generally, DSC does not detect thermal transitions of minor components in a polymer sample, such as those in a blend (i.e. components that are present at levels less than 5%) [10].

Information that can be obtained by DSC analysis are shown in *Fig.I. 14* illustrating typical polymer thermograms.

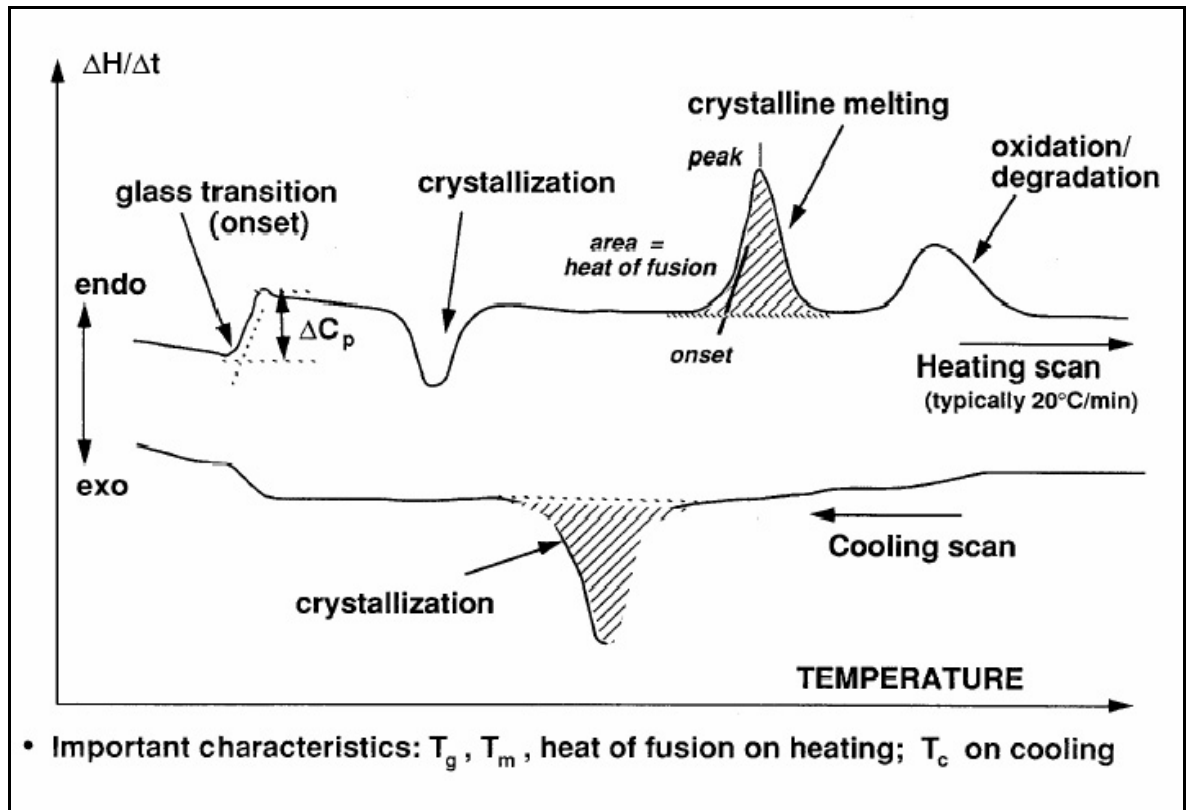


Fig.I. 14 Typical polymer DSC thermogram [20]

Thermal History

The thermal history of a polymer sample can be useful record of the processing conditions that have been used to fabricate it. DSC can be used to probe the thermal history of the polymer by virtue of the correlation between the annealing temperature and temperature of the annealing peak.

Thus, DSC peaks arising due to secondary crystallization can be used as indicator of thermal history (time and temperature), since the melting temperature of these crystallites correlates with the temperature, at which such crystallites were formed [10].

Melting Point

The most often quoted property of semicrystalline polymers, beside their density, is the melting point (T_m). Melting point data are required by polymer fabricators so that they can determine at which temperature the polymers should be processed.

The 'melting endotherm' of polymers is often broad due to variations in crystal thickness, which in turn, can lead a range of melting points since thinner crystals melt at

lower temperatures. The height of the melting endotherm at a given temperature is a measure of the proportion of lamellae possessing that particular melting point. In practice, the true melting point of the polymer is often difficult to obtain because relatively slow heating rates are required for the DSC determination. The use of slow heating rates will only yield a more accurate value for T_m if no reorganization of the sample occurs. However, slow heating rates (less than 60 °C/min) can often lead to annealing effects such as recrystallization and lamellar thickening, which may alter the crystalline characteristics of the sample. As a result, the measured T_m is not characteristic of the original sample. In contrast, if the heating rate is too fast, an erroneously high melting temperature may be obtained due to superheating. Superheating occurs when the heating rate used in the DSC scan exceeds the rate at which the crystalline polymer melts and is a problem particularly with those polymers having thick crystalline domains. When attempting to reduce the heating rate dependence of T_m , a reduction in the sample weight alone is not enough. Instead, reducing the sample thickness and increasing the sample-pan contact area has been proposed. In any case, the shift of T_m due to superheating should be constant for a given polymer if the heating rate and sample mass are fixed [10].

4.2.2 Dynamic Mechanical Thermal Analysis

In viscous systems, all the work done by the system is dissipated as heat, whereas in purely elastic systems all the work is stored as potential energy (as in the spring component of the dashpot and spring model). Polymers, of course, behave in a dual manner, i.e. they exhibit both viscous and elastic behaviors. Dynamic mechanical thermal analysis (DMTA) is an excellent technique for extracting information on dynamic material properties, which relate to these two regimes of behavior. DMTA measurement can give the following properties as a function of temperature:

- the elastic modulus (G') which represents how much energy the polymer stores;
- the viscous modulus (G'') which indicates the polymer's ability to dissipate energy as heat.

These quantities, G' and G'' , are also referred to as the dynamic storage modulus and the dynamic loss modulus, respectively, and in turn relate to the stiffness of the material and to its dampening capacity (energy dissipation). DMTA thus allows the analyst to determine a correlation between the temperature and the modulus of the material. By

using the onset of the modulus curve, the temperature at which a rapid drop in modulus occurs can be determined.

A major advantage of DMTA over DSC is that side-chain and main-chain motion in specific regions of the polymer, as well as local relaxations, can be measured. One should not forget that while the main transition, T_g , is associated with large-scale segmental motion; small, secondary damping peaks are associated with the motion of short segment on the polymer backbone. Thus, the minor transition can yield important information about the polymer, particularly that related to toughness.

Another area of difference is the sensitivity of T_g detection. DSC has sensitivity problems when it comes to detecting the T_g of minor components in a polymer. DMTA, on the other hand, is highly sensitive at detecting transitions since the properties that it measures (namely modulus and the damping factor) vary appreciably from the glassy to the rubbery state. In contrast, there is only a subtle change in specific heat at the T_g and thus DSC is not well suited for detecting these transitions.

Although the DMTA technique is well described in the literature, the analyst needs to recognize that it is important that the sample be properly clamped, in order to avoid resonance affects. A limitation of DMTA is that it cannot measure the mechanical properties of the polymer over the full temperature range, because the sample excessively dampens the applied oscillation as it approaches its softening point [10].

4.3 Durometer Hardness (ISO 868 Shore D measurement)

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation, or scratching. Hardness is purely a relative term and should not be confused with wear and abrasion resistance of plastic materials. Hardness test can differentiate relative hardness of different grades of a particular plastic. However, it is not valid to compare hardness of various types of plastics entirely on the basis of one type of test, since elastic recovery along with hardness is involved. The test is further complicated by a phenomenon such as creep. Many tests have been devised to measure hardness. Since plastic materials vary considerably with respect to hardness, one type of hardness test is not applicable to cover the entire range of hardness properties encountered. Two of the most commonly used hardness tests for plastics are the Rockwell hardness test and the Durometer hardness test.

The Durometer hardness test is the mostly used for measuring the relative hardness of soft materials. The test method is based on the penetration of a specified indenter forced into the material under specified conditions.

The Durometer hardness tester consists of a pressure foot, an indenter, and an indicating device. The indenter is spring loaded and the point of the indenter protrudes through the hole in the base. The test specimens are at least thick 1/4-in. thick and can be either molded or cut from a sheet. Several thin specimens may be piled to form a 1/4-in. - thick specimen but one-piece specimens are preferred. The poor contact between the thin specimens may cause results to vary considerably. The test is carried out by first placing a specimen on a hard, flat surface. The pressure foot of the instrument is pressed onto the specimen, making sure that it is parallel to the surface of the specimen. The durometer hardness is read within 1 sec after the pressure foot is in firm contact with the specimen. Two types of durometers are most commonly used - type A and type D. The basic difference between the two types is the shape and dimension of the indenter. The hardness numbers derived from either scale are just numbers without any units. Type A durometer is used with relatively soft material while type D durometer is used with slightly harder material [21].

II. EXPERIMENTAL

5 SAMPLE PREPARATION

5.1 Materials

Commercially available isotactic polypropylene MOSTEN 58412, produced by Chemopetrol Litvinov a.s., Czech Republic, is homopolymer, with middle distribution of molecular weight M_w about 170000. It is multipurpose material, suitable for injection molding, production of belts, ropes and cords, as well as sheets intended for subsequent thermoforming. Some characteristics of this material featured by producer are shown in *Tab.II. 1*.

Tab.II. 1 Characteristics of PP MOSTEN 58412

Property	Unit	Typical merit	Test method
Melt flow index (230/2.16)	g/10 min	3.3	ISO 1133
Density	kg/m ³	914	ISO 1183
Yield stress	MPa	34	ISO 527
Ultimate strength	MPa	22.5	ISO 527
Elongation at yield	%	7.6	ISO 527
Elongation at break	%	280	ISO 527
Flexural E-modulus	MPa	1450	ISO 178
Tension E-modulus	MPa	1600	ISO 527
Impact toughness Charpy +23°C	kJ/m ²	6	ISO 179
Softening temperature from Vicat	°C	157	ISO 360
Hardness Shore D	-	66	ISO 868
Melting temperature	°C	155 - 168	ISO 11357
Isotacticity index	%	98.5 - 99	ISO 9113

In order to increase the β -phase content in the samples, specific β -nucleating agent (NJ Star NU100), produced by RVI International, was used. It is *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide; its chemical formula is shown in *Fig.II. 1*.

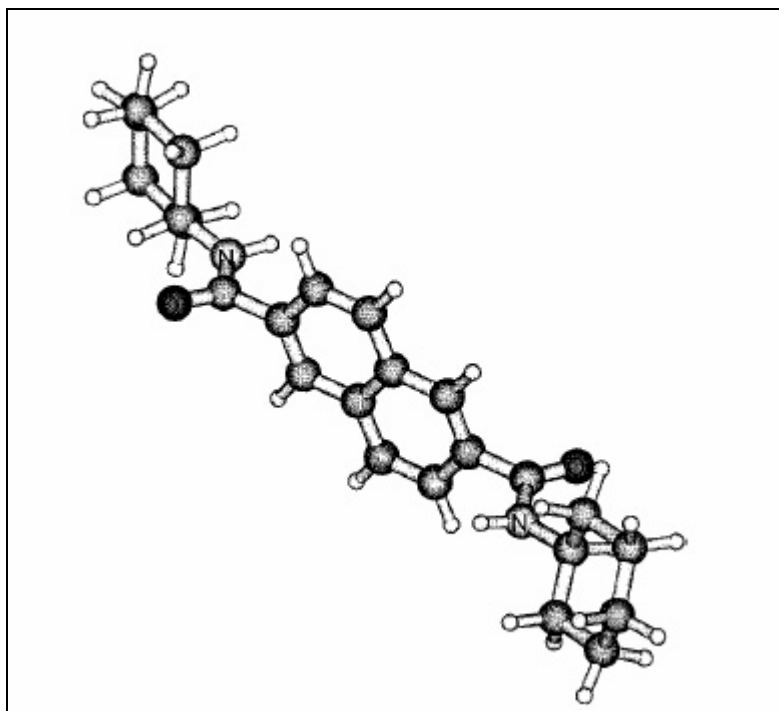


Fig.II. 1 Molecular model of N,N'-dicyclohexyl-2,6-naphthalenedicarboxamide, the β -nucleant used in this work [22]

5.2 Blends

A Brabender DSK 42/6D twin screw extruder was used for preparation and homogenization of blends containing PP Mosten 58412, NU100 nucleating agent and 0.3 wt.% of paraffin oil for better dispergation of the nucleating agent. The composition of the blends is given in *Tab.II. 2*.

Tab.II. 2 Composition of blends

Blend no.	wt.% NU100	wt.% PP	wt.% paraffin oil
1	0	100	0
2	0.01	99.69	0.3
3	0.03	99.67	0.3

5.3 pvT device

A pressure-volume-temperature (pvT) technique was used for samples preparation (i.e. high-pressure crystallization) and for obtaining the crystallization information (namely time, piston position, temperature and pressure) used for measuring of the crystallization kinetics.

The sample is put into a cylindrical cell, and the specific volume is deduced from measurement length of the sample. The experimental results of this work were obtained with a pvT100 apparatus manufactured by SWO Polymertechnik GmbH (Krefeld, Germany). A schema of this device is shown in *Fig.II. 2*. The diameter of the cell is 7.8 mm. The lower piston is fixed, and the upper one can move, ensuring the pressure. A PTFE sealing was put between each piston and the sample to avoid a leakage of the melt. The measurement of the upper piston displacement provides a length of sample after subtraction of the sealing volume. Temperature control of the cell is ensured by an electric heater band, and the cooling is by air. The temperature is measured using a thermocouple placed near the sample, even if it sticks on the cell.

This technique's main disadvantage is an inexact determination of hydrostatic pressure on a sample in the solid state. However, according to ref. [23] it can be concluded that for our purpose, the error rising from non-hydrostatic pressure is very small. The problem would obviously be more important for a glassy material with lower Poisson coefficient and higher yield stress.

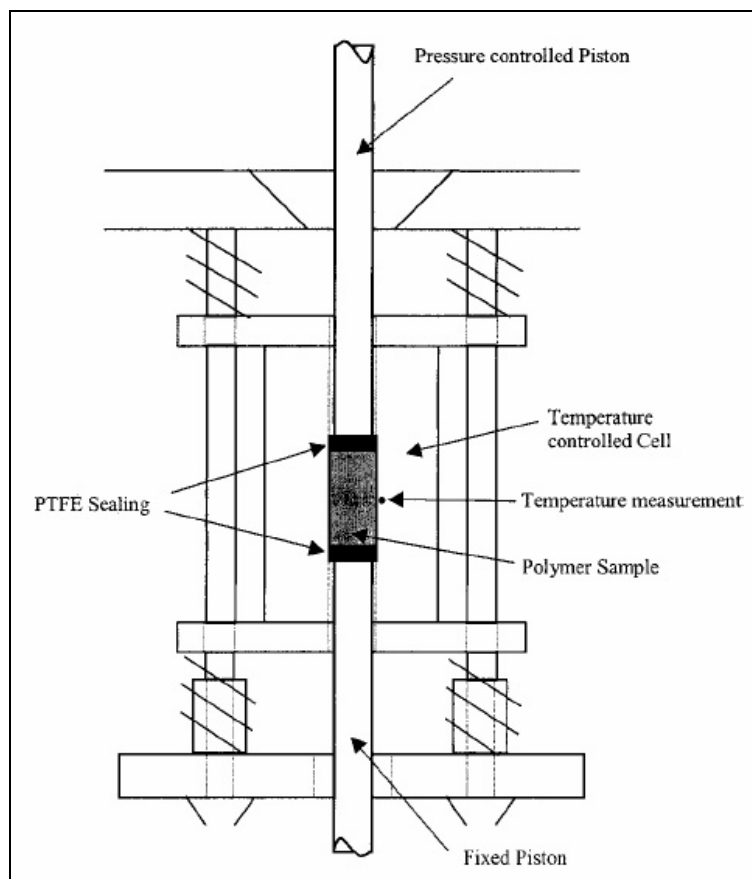


Fig.II. 2 Schema of the pvT cell [23]

5.4 Samples measured by the pvT system

Approx. 0.75 g of the material was put into a measurement cylinder and melted at the temperature of 240°C and 20 MPa pressure for 7 minutes. Then, the crystallization pressure was introduced and the material was cooled down at rate 5 °C/min to a given crystallization temperature T_c .

Reaching of this pressure and temperature, a monitoring of isothermal and isobaric crystallization process was started. The end of crystallization was signaled by the piston holding the same position for 5 minutes. Then the sample was quickly cooled to the temperature 50°C and pressure was shifted off.

For non-isothermal isobaric crystallization was used same “melting” process. Subsequently, samples were non-isothermally crystallized at various cooling rates 2, 5 and 20 °C/min under 100 MPa pressure.

The crystallization process was monitored by a computer, which records time, temperature and piston position. Resulting samples was a cylinder with diameter 7.8 mm and length approx. 18 mm.

Following crystallization sets were used:

i) Isothermal isobaric crystallization

Pressure: 50 MPa $T_c = 130, 140, 150, 160\text{ }^{\circ}\text{C}$

100 MPa $T_c = 140, 150, 160, 170\text{ }^{\circ}\text{C}$

150 MPa $T_c = 150, 160, 170, 180\text{ }^{\circ}\text{C}$

200 MPa $T_c = 160, 170, 180, 190\text{ }^{\circ}\text{C}$

Concentrations: 0, 0.01, 0.03 wt.% NU100

ii) Non-isothermal isobaric crystallization

Pressure: 100 MPa

Cooling rates: 2, 5, 20 $^{\circ}\text{C}/\text{min}$

Concentrations: 0, 0.01, 0.03 wt.% NU100

5.5 Specimens for WAXS, DMTA and Hardness measurement

Specimens for wide angle X-ray scattering (WAXS) and dynamic mechanical thermal analyzing (DMTA) were cut out from the central part of the samples prepared by high-pressure crystallization. Then, the specimen surface was grinded and polished using water cooled disk-type grinder with sand papers to rectangular shape (*Fig.II. 3*). The specimen dimension was 2 mm thickness, 7 mm width and 19 mm length. After WAXS these specimens were subsequently used for DMTA analyzing and then for Shore D hardness analysis.

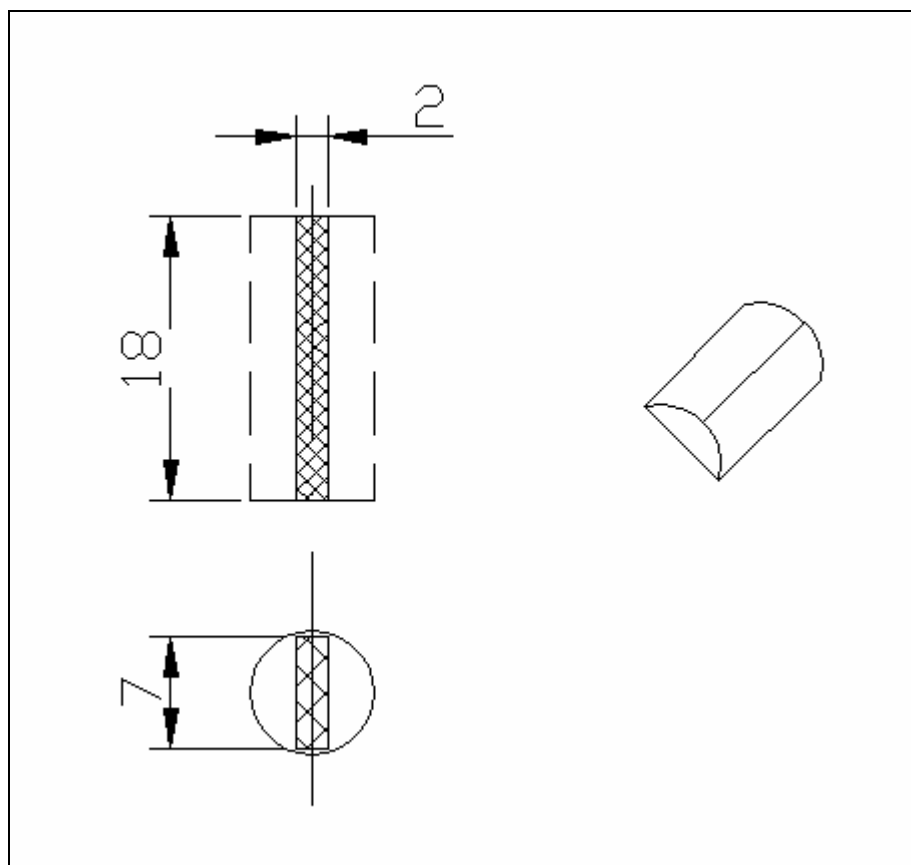


Fig.II. 3 Schema of sample for WAXS, DMTA and SHORE D measurement and sawed off segment

5.6 Specimens for DSC analysis

From central part of the sawed off segments (see *Fig.II. 3*) slices with thickness approx. 100 μm were cut out using a FOK GYEM OE-908 microtome. The slices with weight approx. 5 mg were put to aluminous pan and covered with aluminous cover. The pan and the cover were crimped with a special tool supplied by Perkin-Elmer Co.

5.7 Specimens for Polarized Light Microscopy

Specimens for polarized light microscopy were prepared by the same way as the previous ones from the sawed off segments. Then, they were microtomed to observe the morphology of the samples prepared at strictly controlled conditions. The prepared slices of thickness 50 μm were placed on the slide, dripped by paraffin oil and covered by a mount.

6 ANALYZING METHODS AND DEVICES

6.1 DSC Analysis

For the purpose of this study, a power-compensated differential scanning calorimeter (DSC-Pyris1, The Perkin-Elmer Co., USA) was employed. Nitrogen as a purge gas, was used and constantly passed (20 ml/s) through the heat sink and over the cells. Temperature calibration was performed using indium as a standard.

The prepared specimens were heated from 50°C up to 190°C with heating rate 10°C/min to obtain melting temperatures and enthalpy of heat fusion.

6.2 WAXS

Wide angle X-ray scattering (WAXS) experiments were performed in reflection mode with an URD 6 diffractometer equipped with $\text{CuK}\alpha$. Radial scans of intensity vs. diffraction angle 2θ were recorded in the range of 10° to 30° by steps of 0.04° and length of step scan 5 s.

6.2.1 Evaluation of multi component crystalline systems

An evaluation of the phase composition in $\alpha/\beta/\gamma$ crystalline systems of iPP has not yet been offered in literature. There are only two basis relations for the quantification of 2-phases crystalline systems, namely β/α and γ/α .

In the β/α crystalline system, the β -phase fraction (B) within the crystalline part of iPP is calculated according to Turner-Jones et al.:

$$B = H_{\beta} / (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_{\beta}) \cdot 100\% \quad (7)$$

In the γ/α crystalline system, the γ -phase fraction (G) within the crystalline part of iPP is calculated according to Pae as:

$$G = H_{\gamma} / (H_{\alpha 3} + H_{\gamma}) \cdot 100\% \quad (8)$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, $H_{\alpha 3}$ are the intensities of the (110), (040) and (130) α reflections corresponding to angles $2\theta = 14.20^\circ$; 17.00° and 18.80° , respectively, and H_{β} is the

intensity of the (300) β reflection at $2\Theta = 16.20^\circ$. H_γ is the intensity of the (117) γ reflection at $2\Theta = 20.05^\circ$.

On the basis of Equations (7) and (8) new relations for the evaluation of $\alpha/\beta/\gamma$ crystalline systems can be proposed as follows [24]:

- i) The (117) γ reflection suppressed the α_3 reflection. Indeed, the γ as well as other α reflections interact with the (300) β reflection. Therefore equation (7) should be modified by addition of H_γ as follows:

$$K_\beta = H_\beta / (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta + H_\gamma) \cdot 100\% \quad (9)$$

where K_β implies relative β -phase content in 3-phase crystalline system of iPP.

- ii) Shared content of both α - and γ - phases ($K_{\gamma+\alpha}$) in this crystalline system can be defined as:

$$K_{\alpha+\gamma} = 100 - K_\beta \quad (10)$$

- iii) The mutual relation between α - and γ - phases (G) is calculated from already mentioned Eq. 8. Consequently, the content of α -phase (K_α) or γ -phase (K_γ) can be easily calculated as:

$$K_\gamma = G \cdot K_{\alpha+\gamma} \quad (11)$$

$$K_\alpha = 100 - K_\beta - K_\gamma \quad (12)$$

6.3 Polarized Light Microscopy

In order to study morphology of the crystallized samples, a Zeiss NU microscope was used. The samples were placed on the microscope stage and observed in the thorough polarized light. Micrographs of the observed structure were taken using a SONY F-717 digital camera. Common graphic software was used for editing of final images.

6.4 DMTA

Dynamic Mechanical Thermal Analysis (DMTA) DMTA measured dynamic moduli (in-phase and out-of-phase) in an oscillatory mechanical deformation experiment during a programmed temperature at controlled frequency. *Fig.II. 4* shows DMTA detail of flexure mode [20].

The specimens, isothermally crystallized under 100 MPa pressure, were measured at the temperature 30°C and frequency 1 Hz by a DMA DX 04 T device.

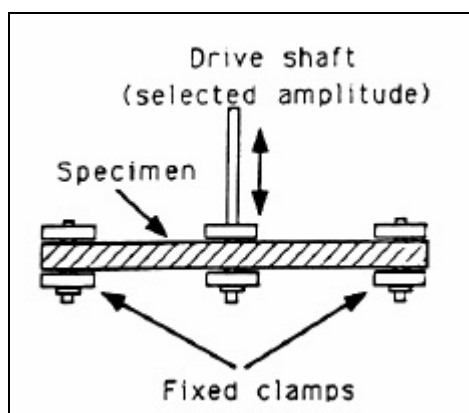


Fig.II. 4 Detail of DMTA in flexure mode

6.5 Hardness Shore D measurement

Standard ISO 868 was used for hardness Shore D measurement of the samples isothermally crystallized under 100 MPa pressure. Shore D hardness values were taken within 15 sec after the pressure foot was in firm contact with the specimen.

III. RESULTS AND DISCUSSION

7 CRYSTALLIZATION KINETICS

It has already been pointed out that the volume changes during crystallization are usually decreasing. This phenomenon can be used to study the kinetics of crystallization. The rate of crystallization increases as the temperature is decreased. This approach has been used for crystallization study also in this work.

7.1 Kinetics of isothermal isobaric crystallization

The analysis of isothermal isobaric crystallization of neat and nucleated iPP blends was carried out by a pvT100 instrument at four different temperatures under four different pressures. Parameters from Avrami equation, n and K , and the halftime of crystallization, $t_{0.5}$, were calculated from dilatometrics data obtained by pvT100, and they are summarized in *Tab.III. 1*. The crystallization halftime, $t_{0.5}$, is defined as the time spent from the onset of crystallization to the point, where the crystallization is 50 % complete. Avrami constant, K , can be taken as a crystallization rate constant.

It should be noted that, according to the original assumption of the Avrami theory, the values of the Avrami exponent n should be an integral ranging from 1 to 4. However, analyses of the experimental data based on the Avrami equation, led to fractional values of n , which cannot be unambiguously assigned to a given type of morphology and primary nucleation type.

Tab.III. 1 Crystallization characteristics of samples at isothermal, isobaric crystallization

Content of NU100 (wt.%)	p (MPa)	T _c (°C)	n	K	t _{0.5} (min)
0	50	130	1.22	3.01E-03	1.4
		140	1.55	5.64E-05	7.3
		150	1.54	3.20E-06	50.0
		160	1.51	5.78E-07	185.0
	100	140	1.08	7.85E-03	1.1
		150	1.54	1.41E-04	3.4
		160	1.69	5.33E-06	18.0
		170	1.82	1.57E-07	75.0
	150	150	1.07	8.77E-03	1.0
		160	1.55	1.73E-04	3.3
		170	1.83	2.60E-06	14.4
		180	2.01	4.21E-08	64.8
	200	160	1.07	8.23E-03	1.0
		170	1.68	5.20E-05	4.7
		180	1.77	2.93E-06	18.0
		190	1.91	1.09E-07	60.0
0.01	50	130	1.02	9.05E-03	1.1
		140	1.67	4.17E-05	5.6
		150	1.54	6.50E-06	30.0
		160	1.16	4.86E-05	62.0
	100	140	1.01	1.27E-02	0.9
		150	1.56	1.50E-04	3.7
		160	1.77	4.02E-06	15.4
		170	1.68	7.46E-07	61.0
	150	150	1.02	1.27E-02	0.9
		160	1.57	1.86E-04	3.2
		170	1.85	2.73E-06	14.0
		180	2.15	2.06E-08	54.0
	200	160	1.11	6.05E-03	1.0
		170	1.66	6.36E-05	4.4
		180	1.86	1.38E-06	20.0
		190	1.75	4.53E-07	57.0
0.03	50	130	0.93	1.69E-02	1
		140	1.03	8.52E-03	1.2
		150	1.33	2.52E-04	6.3
		160	1.68	2.40E-06	30
	100	140	0.75	3.10E-02	1.2
		150	1.04	1.03E-02	1
		160	1.27	7.57E-04	3.7
		170	1.55	1.47E-05	17.4
	150	150	0.93	1.29E-02	1.5
		160	1.06	8.00E-03	1.1
		170	1.23	1.16E-03	3.1
		180	1.48	3.63E-05	13.5
	200	160	1.05	8.84E-03	1.0
		170	1.04	7.52E-03	1.3
		180	1.10	1.81E-03	3.8
		190	1.47	3.23E-05	15.0

Tab.III. 1 shows overall dependence of crystallization halftime, $t_{0.5}$, the rate constant, K , on crystallization temperature, T_c , where $t_{0.5}$ is rising with increasing T_c and the rate constant, K , is decreasing.

For 50 MPa crystallization pressure the effect of nucleating agent, NU100, can be particularly seen – it causes strong decrease of crystallization halftime with rising amount of NU100. At crystallization temperature 160°C, the half-time is $t_{0.5} = 185$ min for neat iPP; for 0.01 wt.% NU100 is 3-times shorter and for 0.03 wt.% NU100 is even 6-times shorter as compared to neat iPP.

At high crystallization pressures – 100, 150, 200 MPa – it can be seen decreasing effect of NU100, particularly at concentration 0.01 wt.% - the crystallization halftimes are very close to the half-times of neat iPP. On the other hand, amount of 0.03 wt.% NU100 still causes 4-times shorter crystallization halftimes compared to neat iPP for high crystallization temperature and rising pressure.

7.1.1 Isothermal crystallization at 100 MPa pressure

For intimate discussion of high-pressure crystallization behavior, the samples crystallized at 100 MPa have been chosen. Crystallization curves of neat iPP samples, and samples nucleated with 0.01 and 0.03 wt.% NU100 are shown in *Fig.III. 1*, *Fig.III. 2* and *Fig.III. 3*. The percent of crystallinity as a function of crystallization time is illustrated.

The crystallization curves of neat iPP samples and samples with 0.01 wt% NU100 possess an analogous form, but the overall times are slightly longer for neat iPP. Neat iPP samples crystallized at the highest crystallization temperature ($T_c = 170^\circ\text{C}$) shows kind of induction period caused by the fluctuation of homogeneous nuclei.

The crystallization curves of samples containing 0.03 wt.% NU100 have different shape – they are narrower and sharper, and overall crystallization times are more than twice shorter as compared with neat iPP.

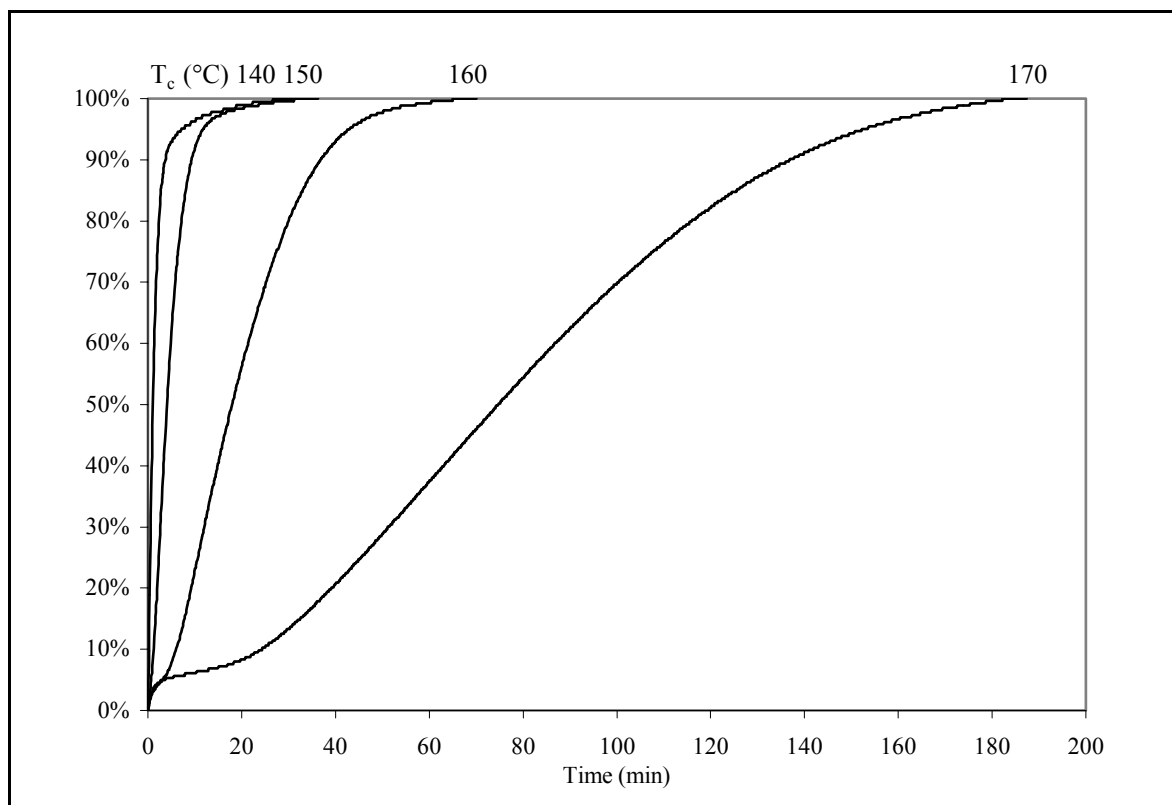


Fig.III. 1 Crystallization curves of the neat iPP samples crystallized at different crystallization temperatures under 100 MPa pressure

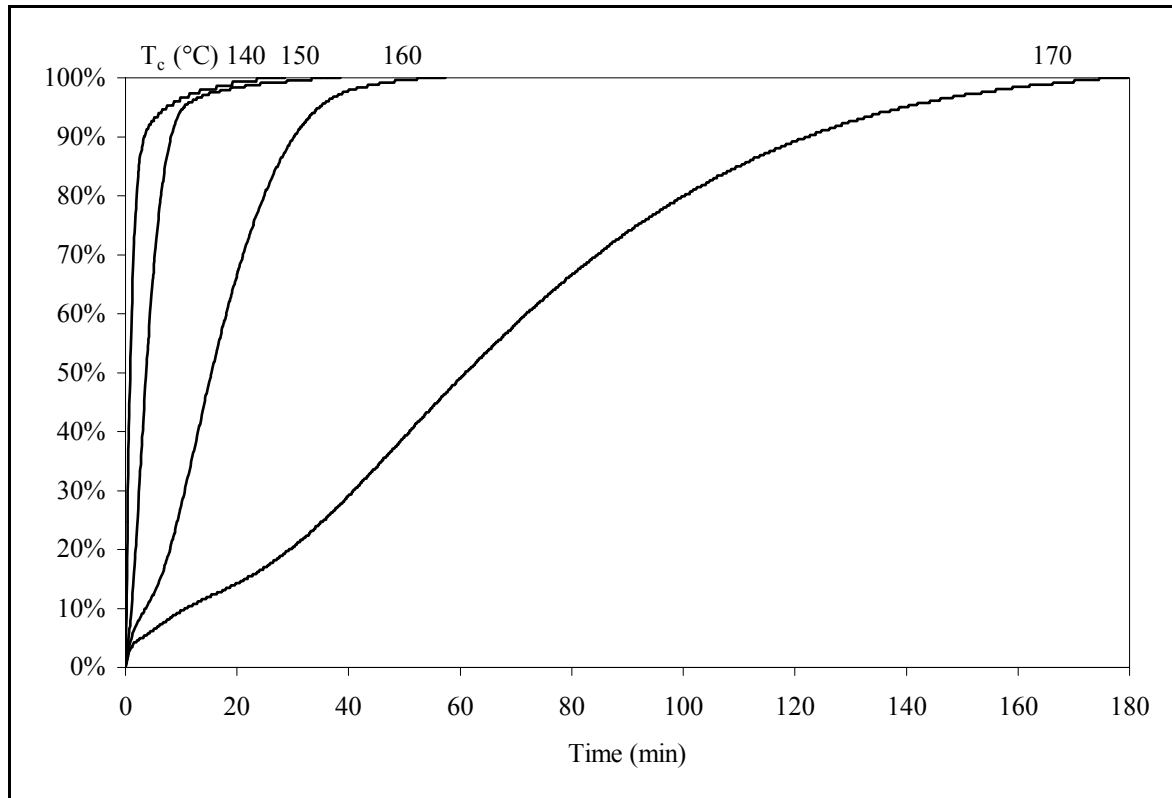


Fig.III. 2 Crystallization curves of the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

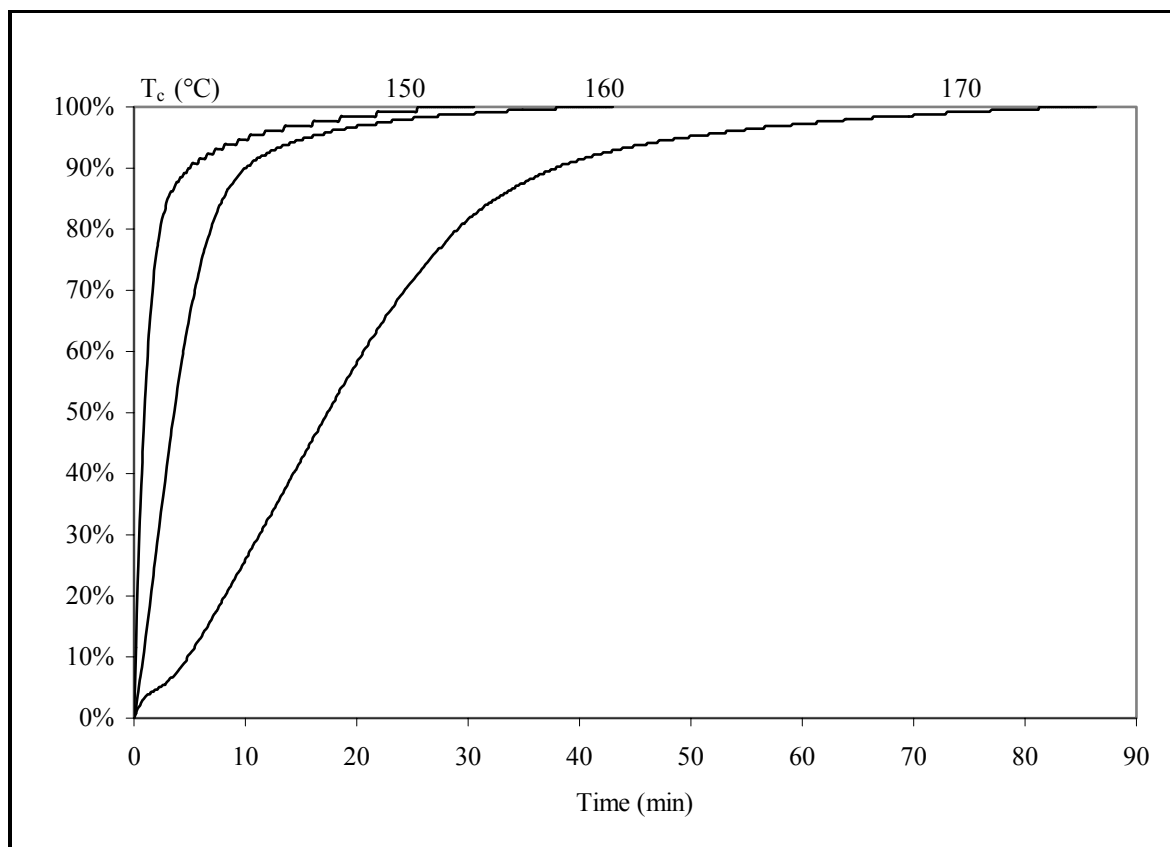


Fig.III. 3 Crystallization curves of the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

Dependences of K rates and crystallization halftimes, $t_{0.5}$, on crystallization temperature, T_c , are illustrated in *Fig.III. 4*, *Fig.III. 5* and *Fig.III. 6*. For better visualization, the K is plotted in log scale. In all cases, K depends on the crystallization temperature, with increasing temperature the K is decreasing. Logically, the crystallization halftime $t_{0.5}$ also depends on the crystallization temperature; with increasing temperature, the crystallization halftime is exponentially rising.

Fig.III. 4, *Fig.III. 5* and *Fig.III. 6* show decreasing crystallization halftime with rising amounts of the nucleant NU100. What can be seen is particularly significant drop of the halftime in samples containing 0.03 wt.% NU100 especially at higher crystallization temperatures.

It is interesting to compare the K constants (in log scale) of individual samples. While the K constant related to the neat iPP samples decreases proportionally with rising T_c , the situation is inverse in the nucleated samples. This can be related to a competitive

growth of each crystalline phase, which is logically more pronounced in the nucleated samples.

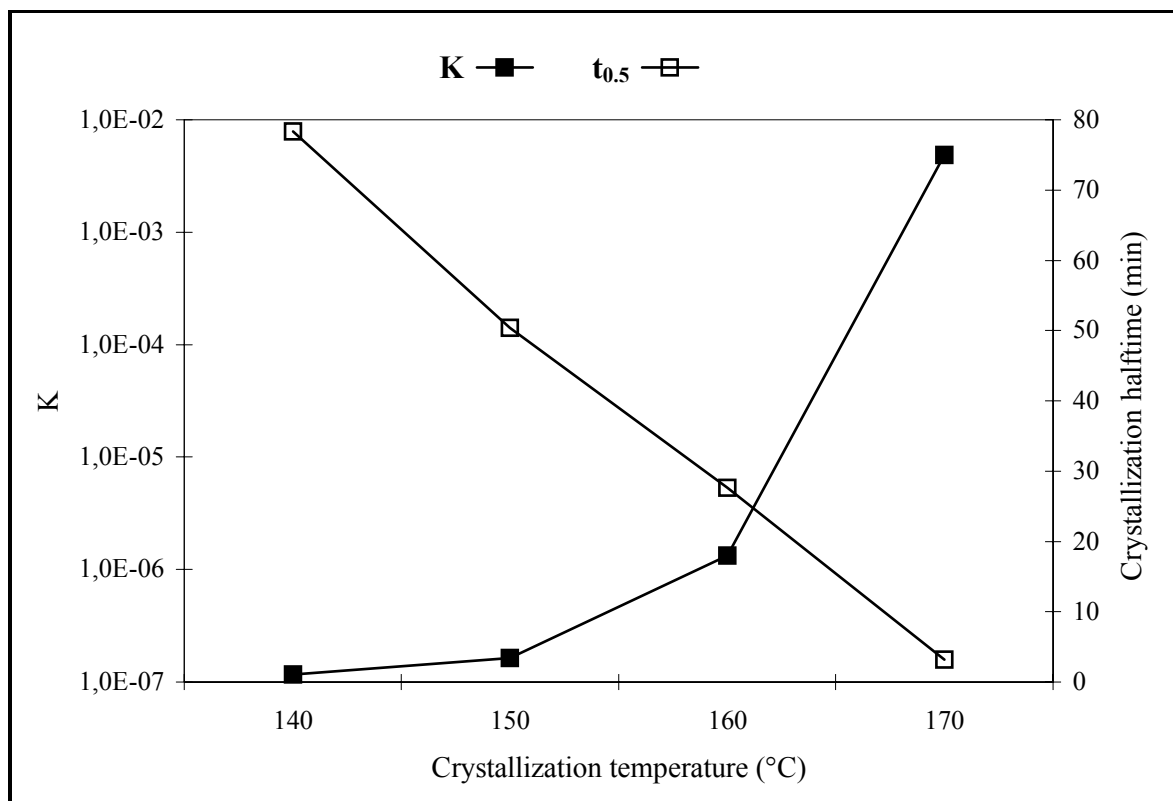


Fig.III. 4 Dependence of K constant (in log scale) and crystallization half-time on crystallization temperature of the neat iPP samples

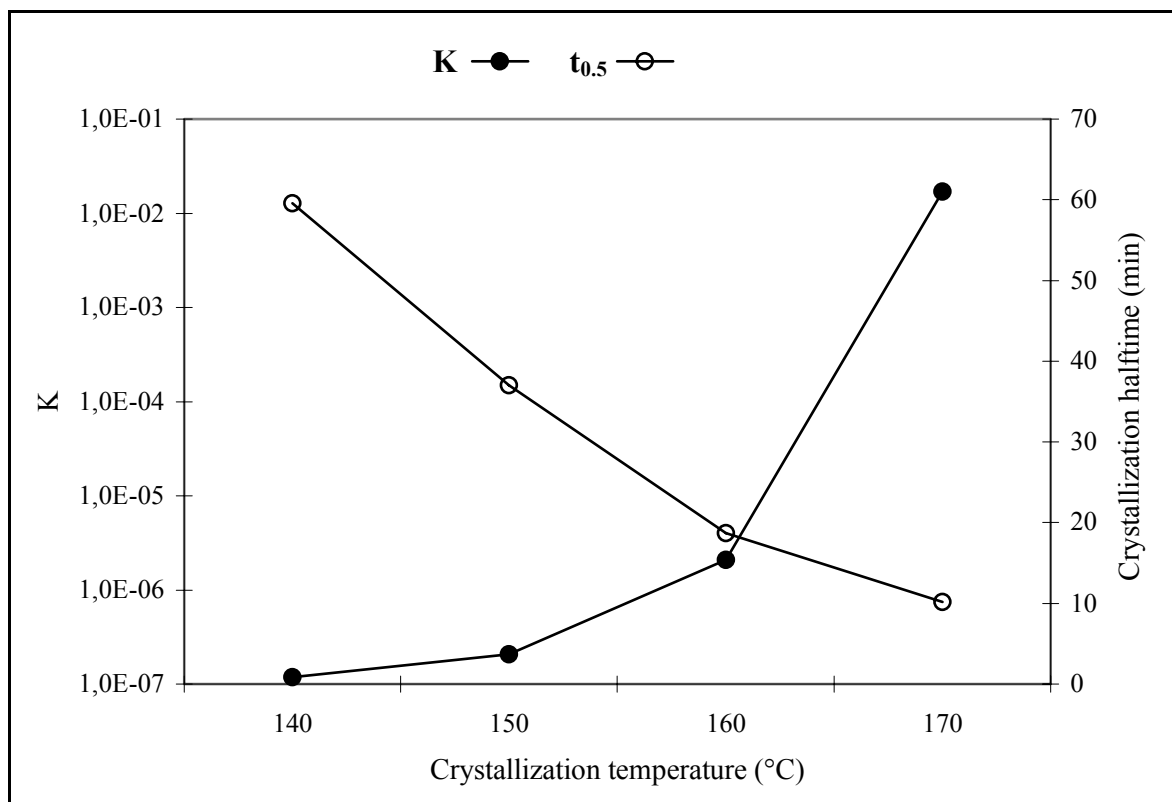


Fig.III. 5 Dependence of K constant (in log scale) and crystallization half-time on crystallization temperature of the samples containing 0.01 wt.% NU100

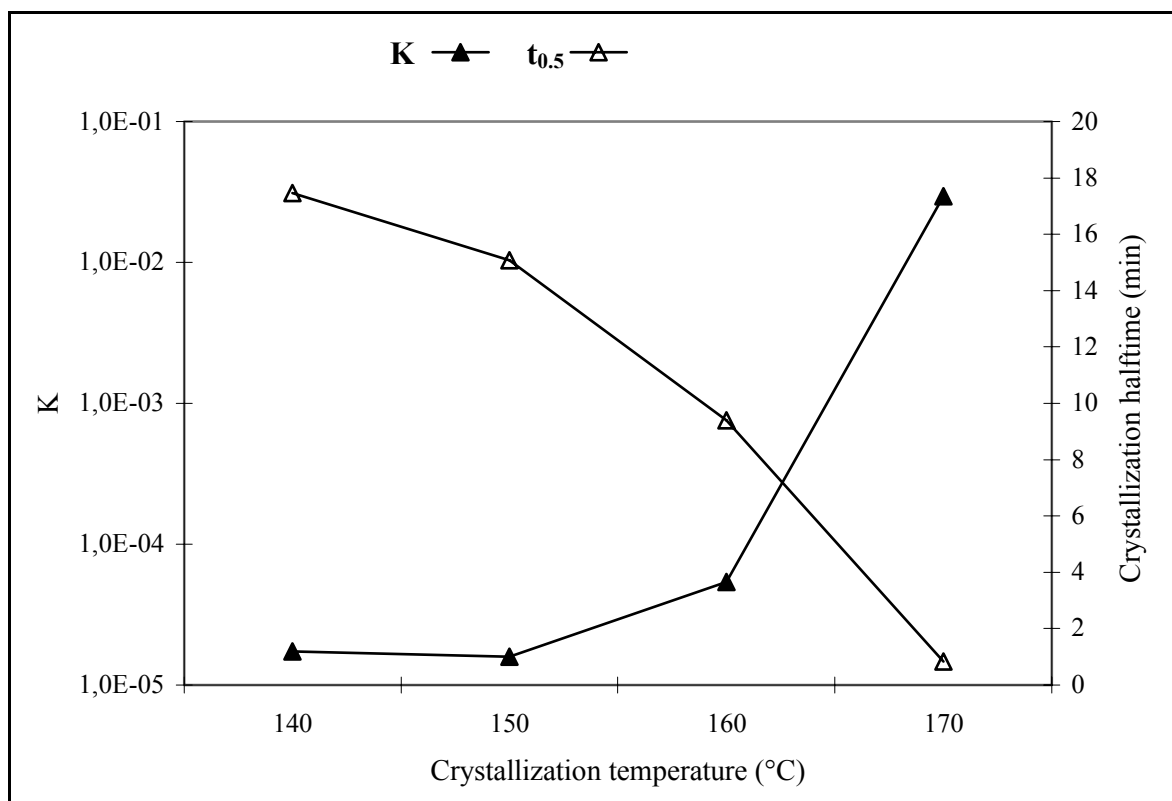


Fig.III. 6 Dependence of K constant (in log scale) and crystallization half-time on crystallization temperature of the samples containing 0.03 wt.% NU100

Fig.III. 7 shows dependence of exponent n on crystallization temperature for samples crystallized under 100 MPa pressure. In all cases, rising crystallization temperature increases the value of exponent n . This is quite surprising, because, originally, the exponent n should not vary with temperature. In addition, the exponents n were not integer numbers and their assignment to a given type of growth has to be very careful.

Again, an interesting situation has occurred. Samples containing 0.03 wt.% NU100 possess quite proportional dependence on the crystallization temperature on the contrary to the sample with 0.01 wt.% NU100 and neat iPP sample. In, addition, the n exponent for sample with 0.03 wt.% is lower as compared to the other samples. This probably reflects different nucleation and growth mechanism.

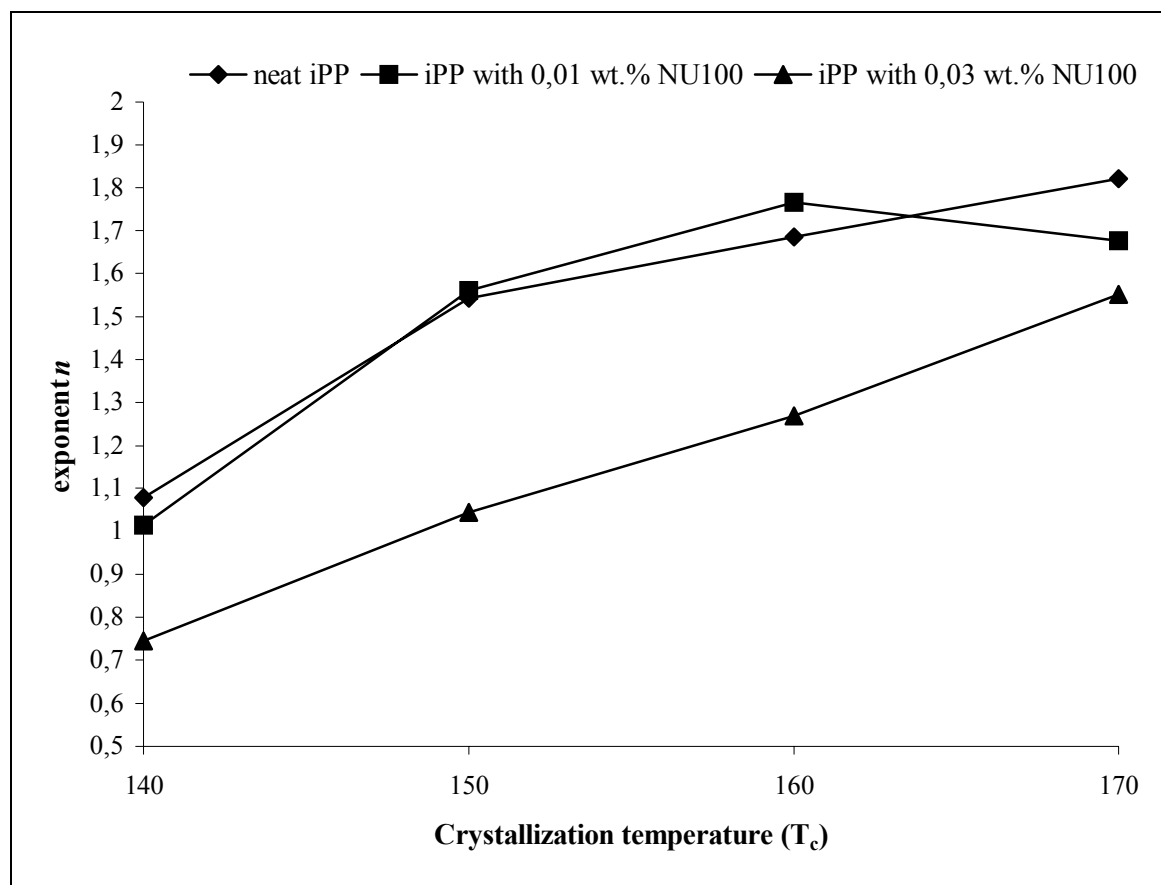


Fig.III. 7 Dependence of exponent n on crystallization temperature for samples crystallized under 100 MPa pressure

7.2 Non-isothermal, Isobaric Crystallization Kinetics

To observe kinetics of non-isothermal isobaric crystallization, the samples containing different amounts of the nucleant were crystallized at 100 MPa and various cooling rates.

In all cases (see *Fig.III. 8*, *Fig.III. 9* and *Fig.III. 10*), the crystallization process is strongly sensitive to the effect of cooling rate; crystallization temperature decreases with higher cooling rate.

From comparing of *Fig.III. 8* and *Fig.III. 9* – neat and nucleated samples of iPP – it can be seen that the addition of 0.01 wt.% NU100 causes increase of crystallization temperature approx. 10°C as compared to neat iPP samples. Really specific situation occurred in samples nucleated by 0.03 wt.% NU100 (see *Fig.III. 10*), there is quite similar behavior as compared to neat iPP samples. This phenomenon can be probably attributed to the competitive crystallization, as already observed by Ref. [32]. The polymorphic composition of such prepared samples will be described thereafter.

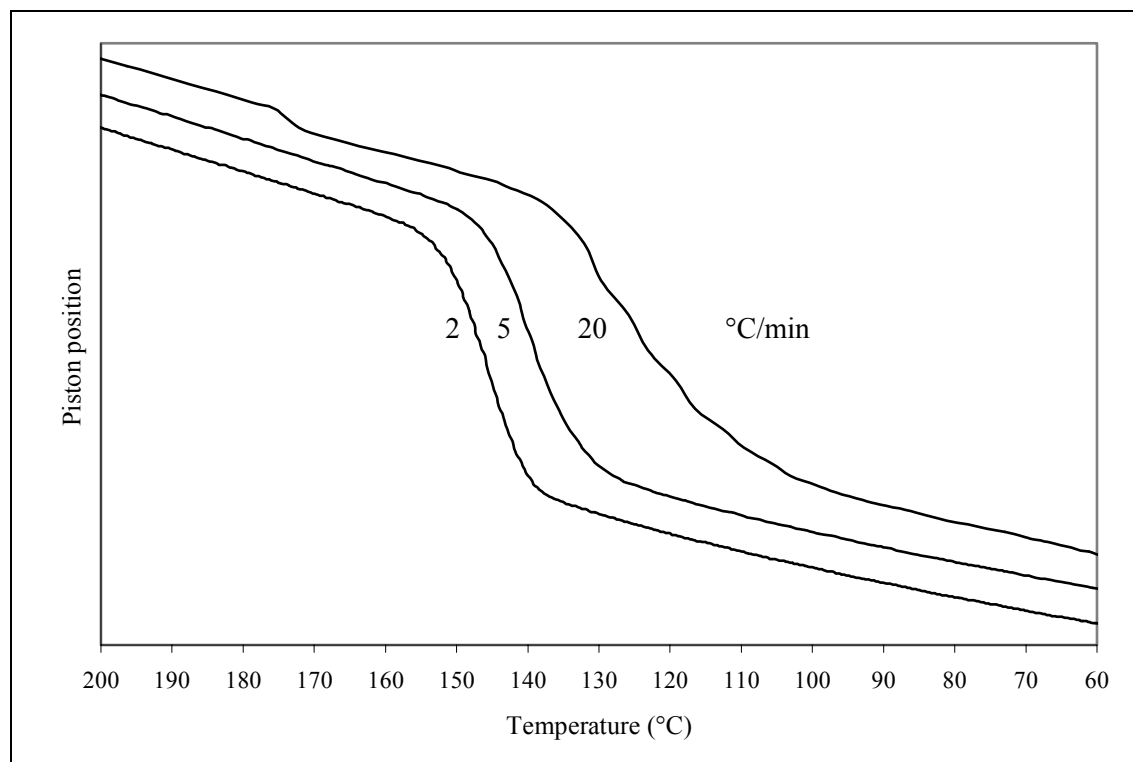


Fig.III. 8 Crystallization curves of the neat iPP samples crystallized under 100 MPa pressure with different cooling rates

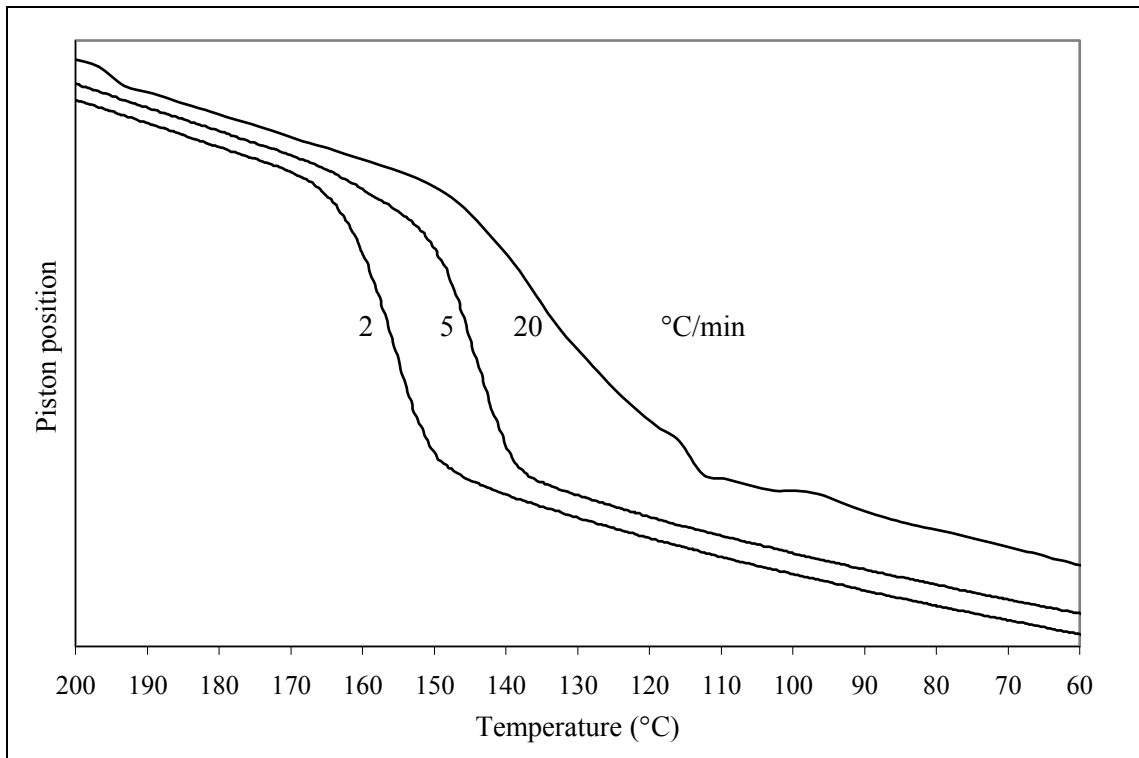


Fig.III. 9 Crystallization curves of the samples containing 0.01 wt.% NU100 crystallized under 100 MPa pressure with different cooling rates

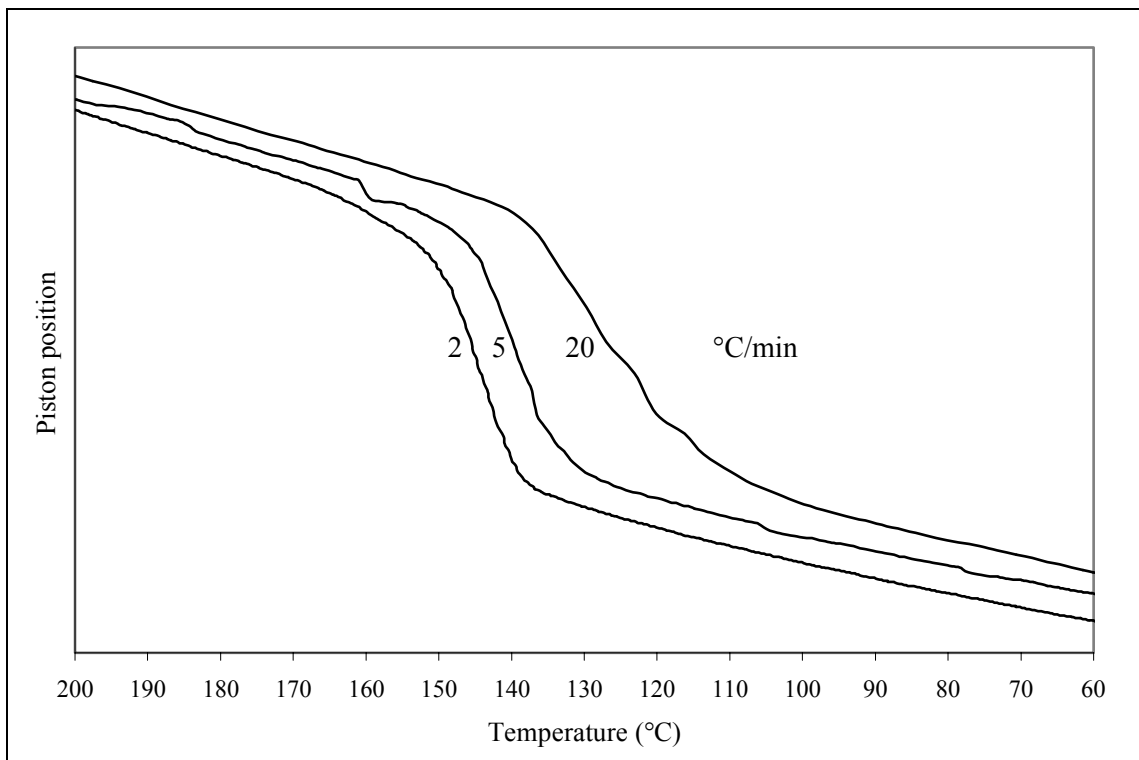


Fig.III. 10 Crystallization curves of the samples containing 0.03 wt.% NU100 crystallized under 100 MPa pressure with different cooling rates

8 POLYMORPHIC COMPOSITION

Polymorphic composition of the samples was observed by WAXS and is figured out as the following percentage graphs.

8.1 Crystallization pressure of 50 MPa

Fig.III. 11 shows that the neat iPP samples consisted of only α - and γ - phases; β -phase was not observed. At this (low) pressure, α -phase is predominant within the crystalline phase.

Fig.III. 12 presents the phase composition of the samples nucleated by a minute amount of the nucleant (i.e. 0.01 wt.%). What can be seen is 3-phase crystalline system in iPP; however the content of γ -phase is rather low and only slightly rises with rising T_c . β -phase is predominant at temperatures of 140 and 150°C, and with rising temperature ($T_c = 160^\circ\text{C}$) its content rapidly decreases at the expense of α - and partially γ - phase growth.

Samples containing 0.03 wt.% NU100 (see *Fig.III. 13*) possess high β -phase content - particularly at lower T_c , β -phase is predominant. Higher amounts of α -phase were obtained at the highest crystallization temperature. At this temperature the β -phase content falls rapidly down. Consequently, the crystalline phase contains even lower amount of β -phase as compared to the sample with 0.01 wt.% NU100. This effect has already been observed [32] and can be assigned to $\beta\alpha$ growth transition during iPP crystallization [33]. The content of γ -phase is in both nucleated samples virtually insignificant.

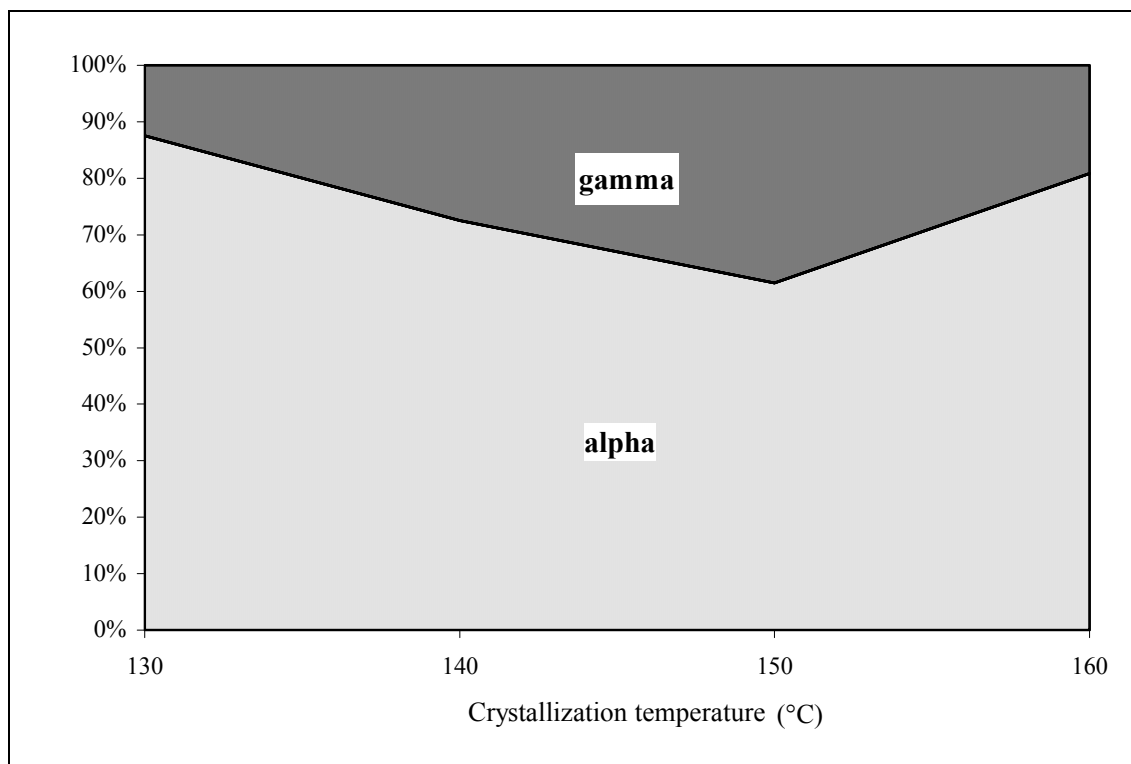


Fig.III. 11 Polymorphic composition in the neat iPP samples crystallized at different crystallization temperatures under 50 MPa pressure

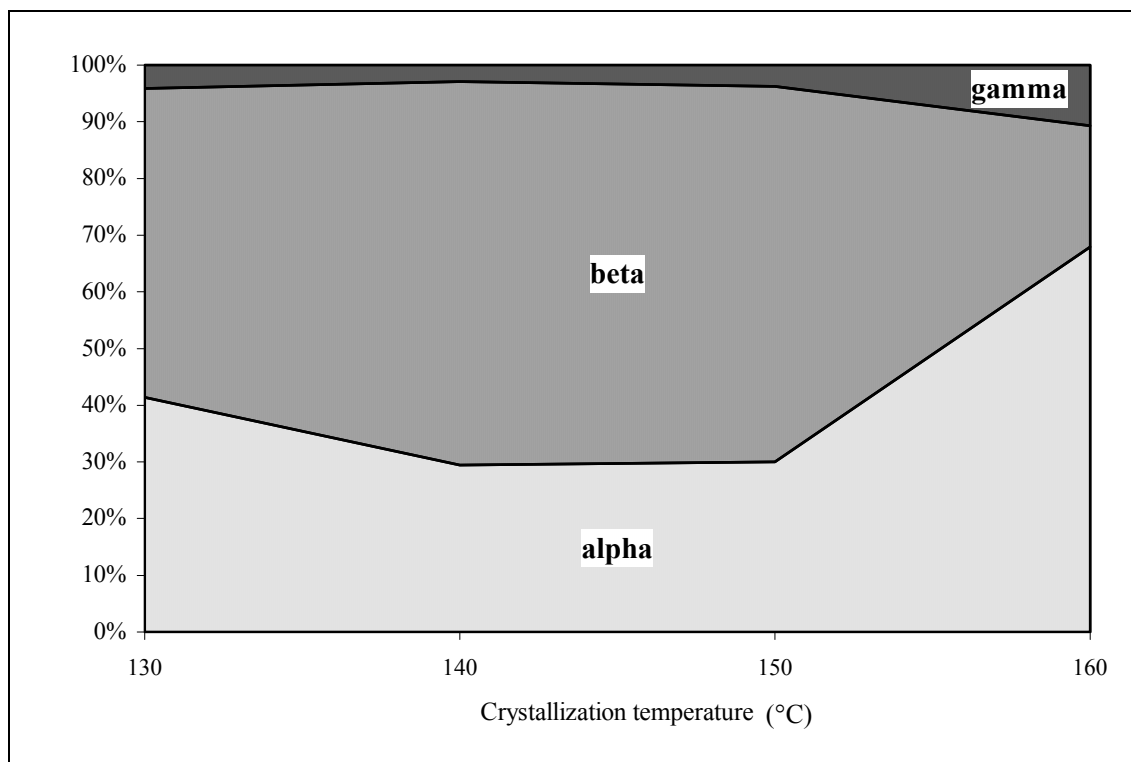


Fig.III. 12 Polymorphic composition in the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 50 MPa pressure

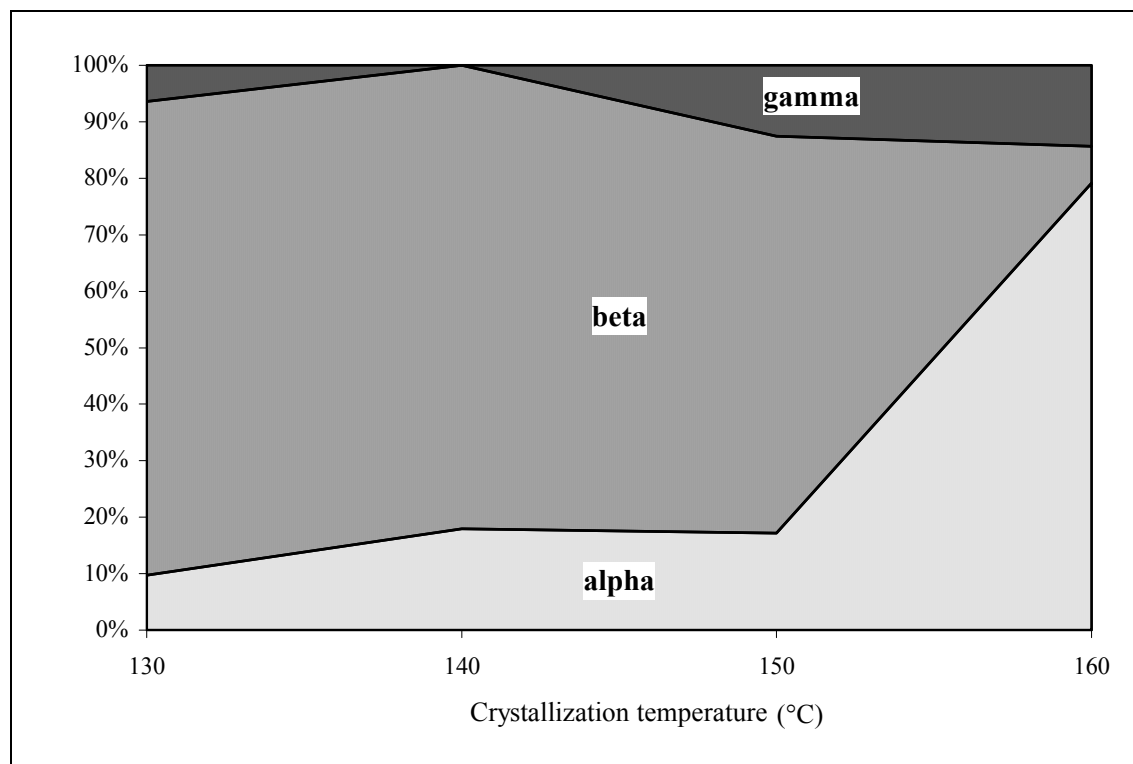


Fig.III. 13 Polymorphic composition in the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 50 MPa pressure

8.2 Crystallization pressure of 100 MPa

By the application of elevated pressure during iPP crystallization, the situation is entirely different. In all samples, the polymorphic compositions of which are illustrated in *Fig.III. 14*, *Fig.III. 15* and *Fig.III. 16*, the γ -phase content increases with rising T_c and becomes predominant at $T_c = 170^\circ\text{C}$.

In *Fig.III. 14* (neat iPP sample) the α -phase content decreases the most in temperature range between 140 and 160°C (from 52 % to 12 %), quite same in *Fig.III. 15* (from 44 % to 10 %) illustrating the polymorphic composition of sample with 0.01 wt.%. These systems consist of virtually similar α -phase content – it follows that β -phase in the sample with 0.01 wt.% is formed at the expense of γ -phase.

In the samples with 0.03 wt.% NU100 (*Fig.III. 16*) the content of α -phase is low (4 – 7 %), but constant in whole temperature range. Volume of γ -phase rises with increasing temperature and becomes predominant at $T_c = 170^\circ\text{C}$. Strong effect of β -nucleant is dominant only at low crystallization temperatures (i.e. 140 and 150°C) at which the β -

phase content is constant (approx. 55 %); at higher temperatures the β -phase content is notably decreasing to 12 %, on the contrary to the rising γ -phase content.

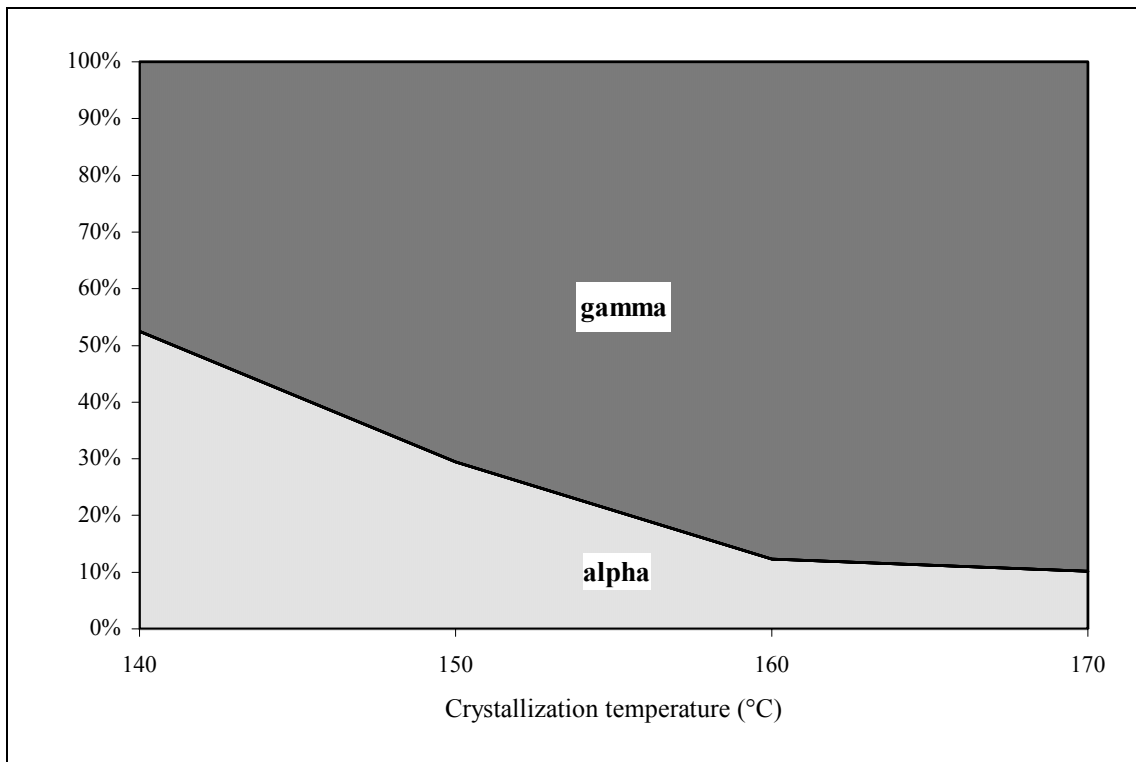


Fig.III. 14 Polymorphic composition in the neat iPP samples crystallized at different crystallization temperatures under 100 MPa pressure

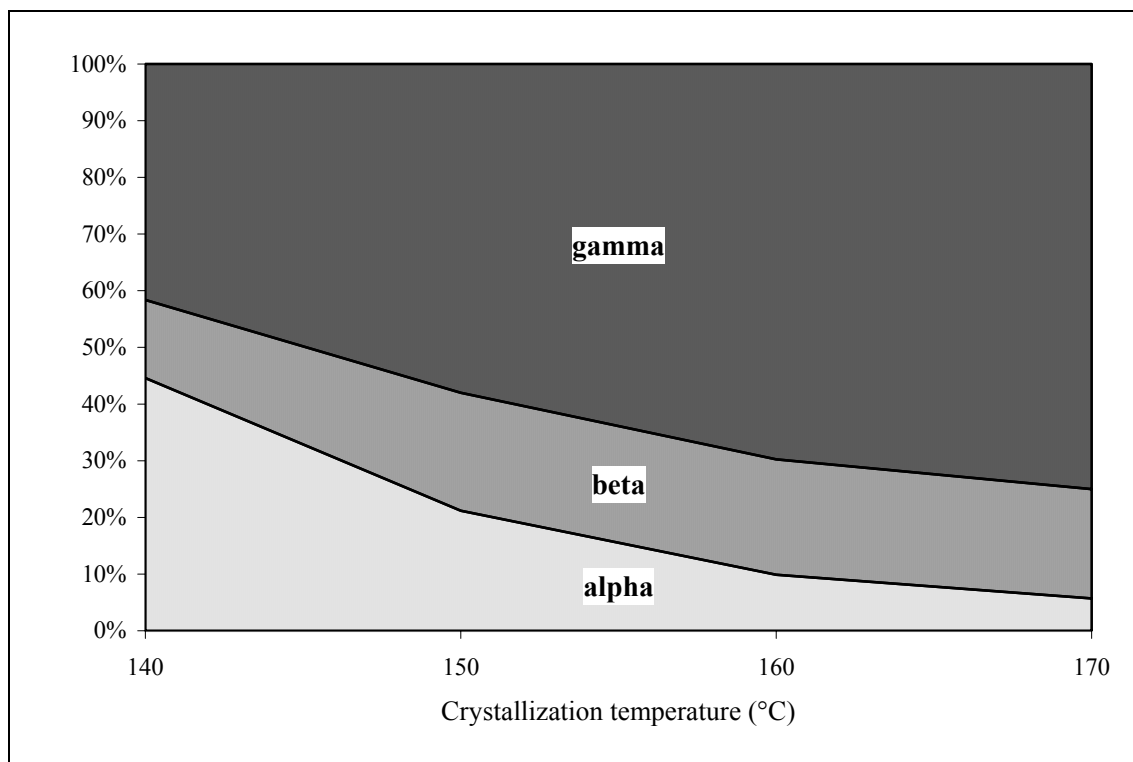


Fig.III. 15 Polymorphic composition in the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

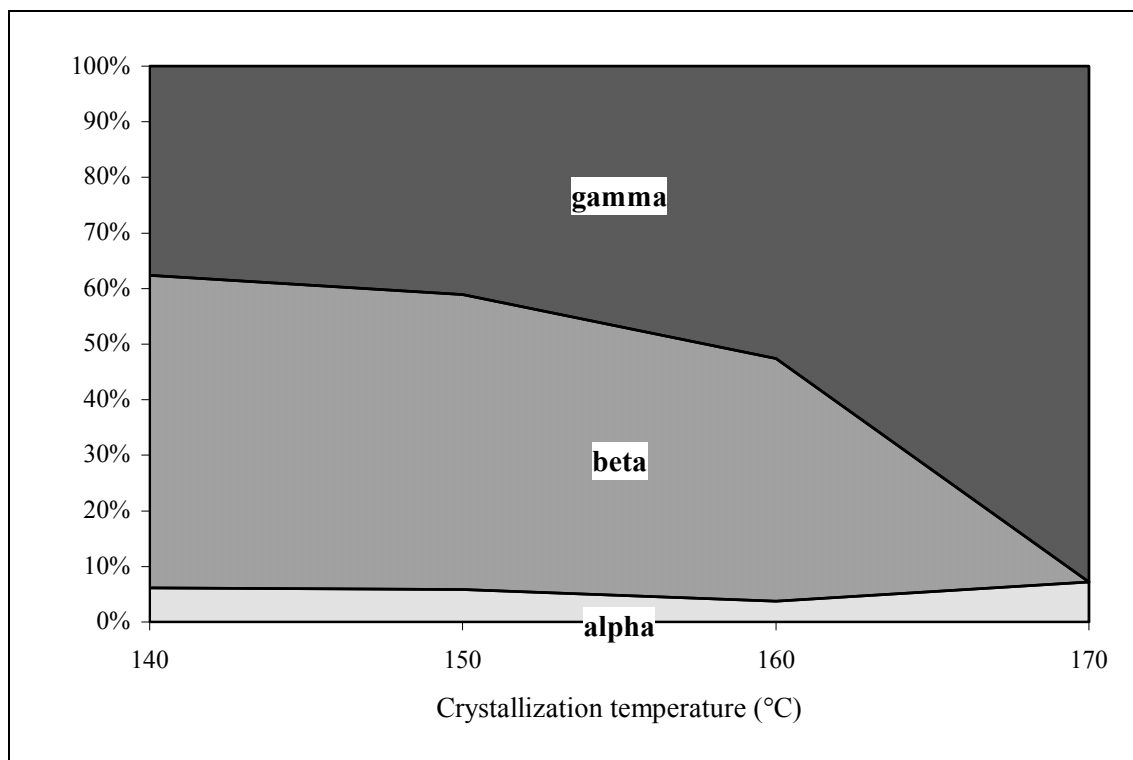


Fig.III. 16 Polymorphic composition in the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

8.2.1 Diffractograms of samples crystallized under 100 MPa pressure

Following diffractograms illustrated in *Fig.III. 17*, *Fig.III. 18* and *Fig.III. 19* correspond to the graphs with polymorphic compositions above and exemplify in detail the changes in the polymorphic composition.

What can be seen in *Fig.III. 17* are typical diffraction spectra of 2-phase (γ/α) crystalline system indicated by the occurrence of both the α_3 (130) and γ (117) diffraction peak, and by the absence of the β (300) peak. The γ peak is more significant at higher temperatures as compared to the α_3 peak; what indicates high content of γ -phase in the neat iPP samples.

The γ -phase was predominant in all samples crystallized at the highest temperature ($T_c = 170^\circ\text{C}$). It should be noted that the polymer crystallized at atmospheric pressure consisted of pure α -phase.

Fig.III. 21 shows characteristic reflections of each crystalline phase – the β peak (300) at 16.20° , the α_3 peak (130) at 18.00° , and the γ peak (117) at 20.05° . Actually, this indicates the formation of 3-phase crystalline system of iPP;

Very specific situation has occurred in *Fig.III. 21* illustrating samples nucleated with 0.01 wt.% NU100. The β reflection has different shape as compared to sample with 0.03 wt.% NU100 (see *Fig.III. 22*). While in the low nucleated sample the β peak appears rising with increasing T_c , the situation is inverse in the case of highly nucleated sample. Again, this can be ascribed to a β/α competitive crystallization and β/α growth transition.

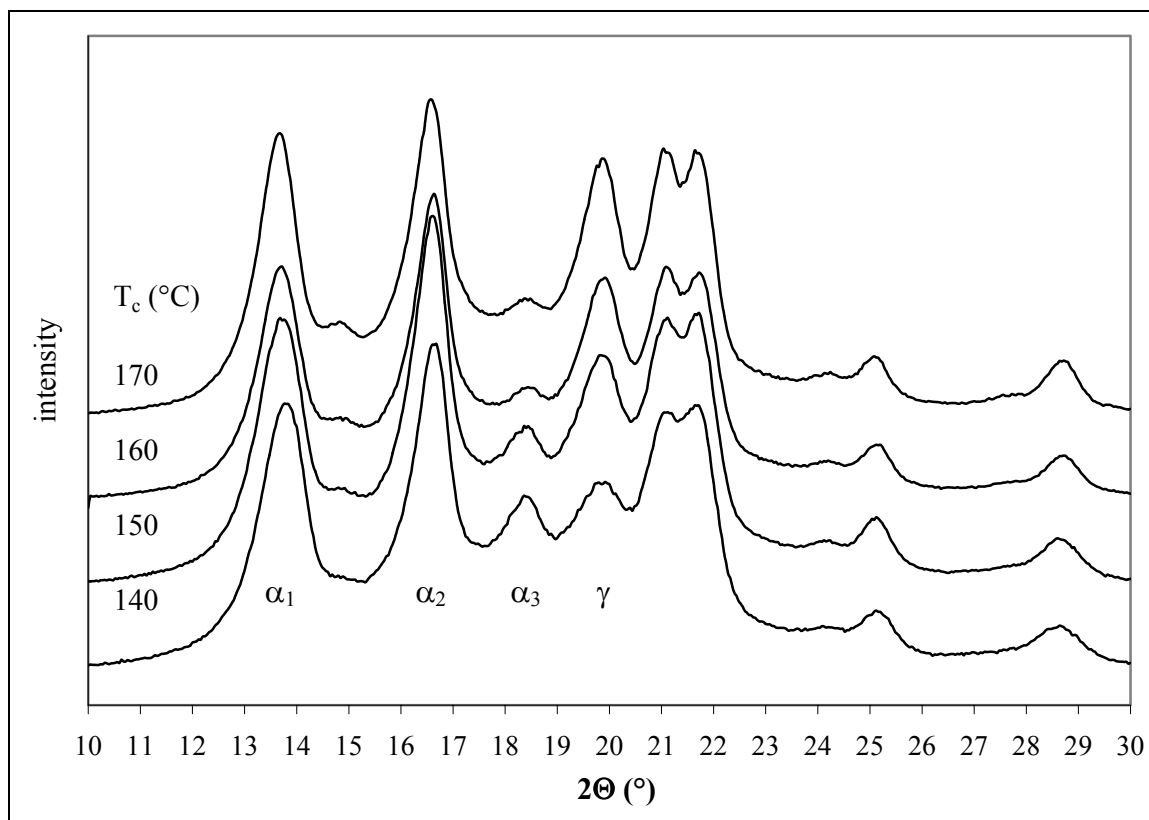


Fig.III. 17 Diffractograms of the neat iPP samples crystallized at different crystallization temperatures under 100 MPa pressure

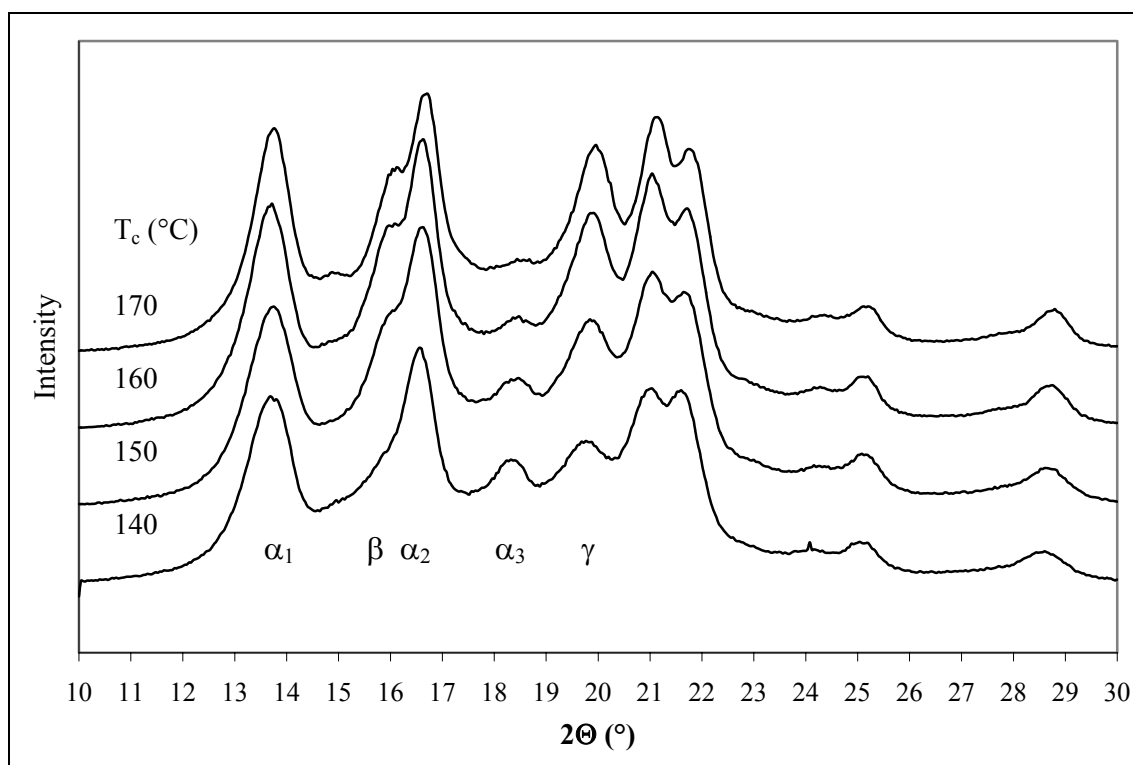


Fig.III. 18 Diffractograms of the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

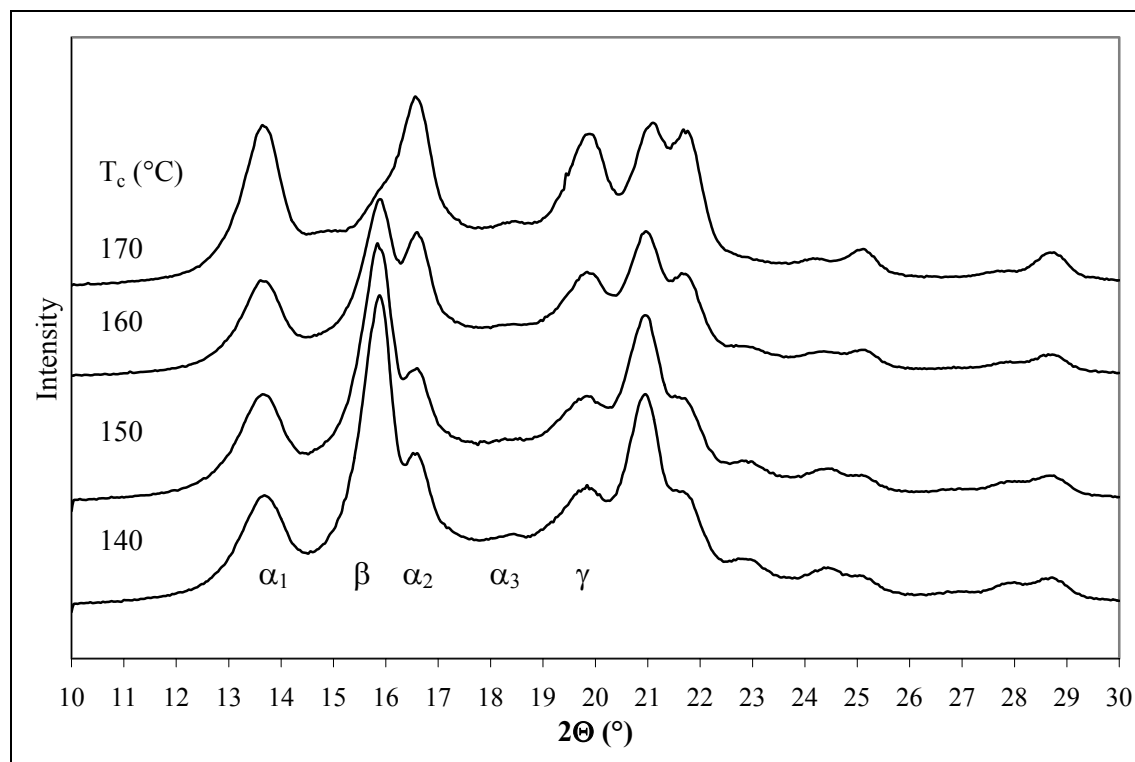


Fig.III. 19 Diffractograms of the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

8.3 Crystallization pressure of 150 MPa

To favor the formation of γ -phase, the crystallization pressure was even more increased. The effect of high crystallization pressure becomes predominant and high amounts of γ -phase is prepared.

In *Fig.III. 20* as well as in *Fig.III. 21* it can be seen decrease of α -phase content with increasing crystallization temperature, and from 170°C temperature up there is less than 2 % of α -phase, and consequently we can talk about pure γ -phase. In the samples with 0.01 wt.% (see *Fig.III. 21*) the effect of β -nucleant is even entirely inhibited by the strong impact of high pressure on iPP crystallization. The polymorphic behavior is quite same as compared to neat iPP.

Interesting phenomenon is shown in *Fig.III. 22* illustrating the polymorphic variation in the samples with 0.03 wt.% NU100. In contrast to samples with 0.01 wt.% NU100, the effect of higher amounts of β -nucleant is able to reduce the strong force of elevated pressure on the γ -phase formation, but only at lower crystallization temperatures.

At these conditions, approx. 30-40 % of β -phase was obtained. At high T_c , on the contrary, the content of γ -phase is predominant again, and both α - and β - phases are entirely suppressed.

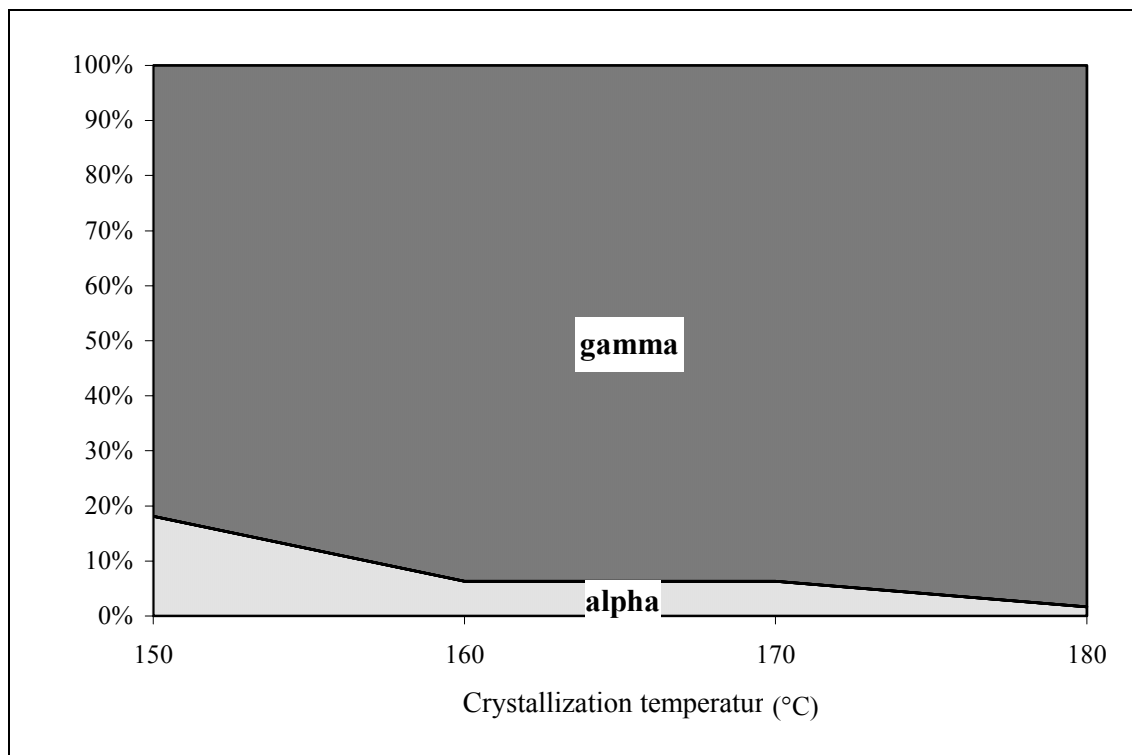


Fig.III. 20 Polymorphic composition in the neat iPP samples crystallized at different crystallization temperatures under 150 MPa pressure

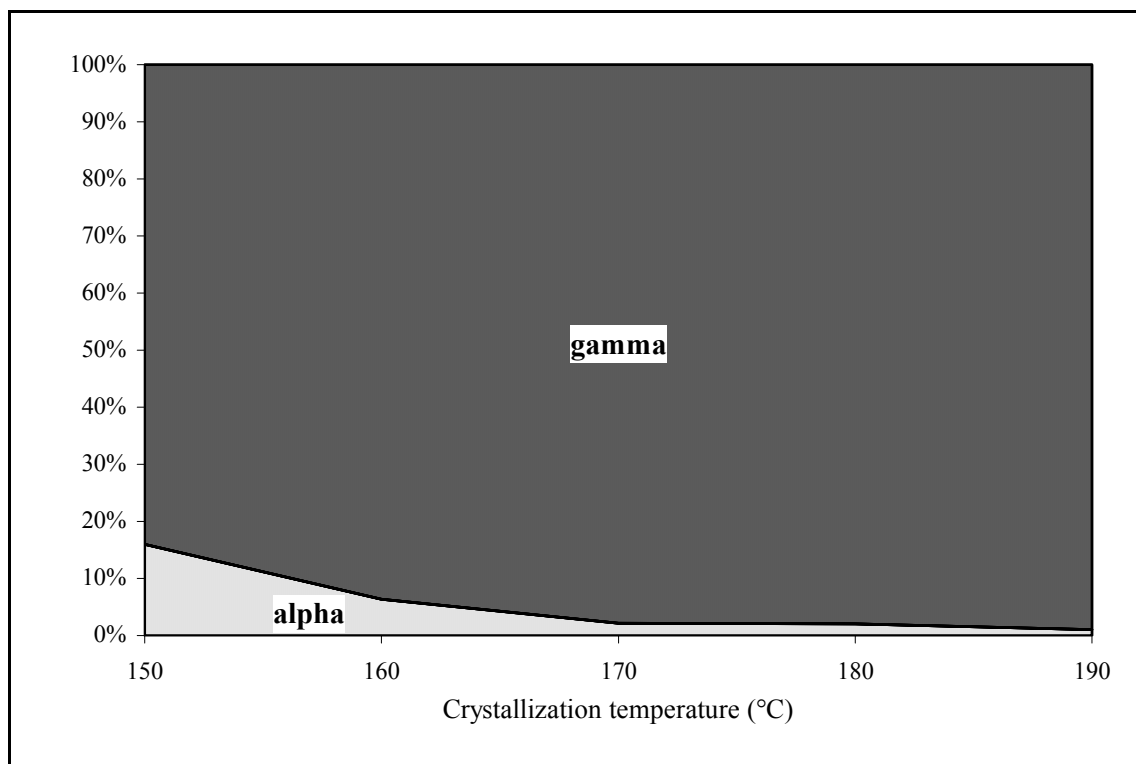


Fig.III. 21 Polymorphic composition in the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 150 MPa pressure

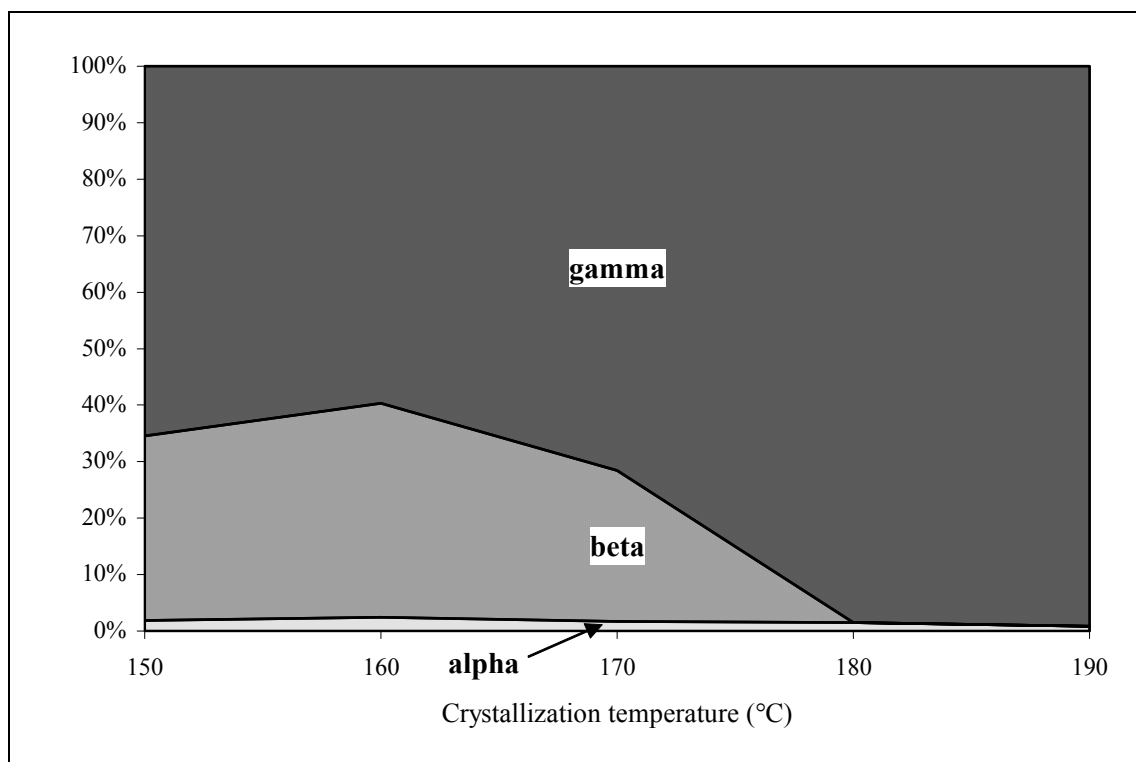


Fig.III. 22 Polymorphic composition in the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 150 MPa pressure

8.4 Crystallization pressure of 200 MPa

The highest crystallization pressure (200 MPa) caused predominant formation of γ -phase, especially in neat and nucleated iPP with 0.01 wt.% NU100 illustrated in *Fig.III. 23* and *Fig.III. 24*. This corresponds with theoretical predictions.

In iPP samples with 0.03 wt.% NU100, *Fig.III. 25*, only small amount of β -phase (approx. 25 %) was obtained at low T_c ; with increasing temperature, namely 180°C, β -phase disappeared totally. Less than 2 % of α -phase are irrelevant so that pure γ -phase was obtained at high T_c . This is further conclusive proof of strong force of high pressure on the crystallization of isotactic polypropylene.

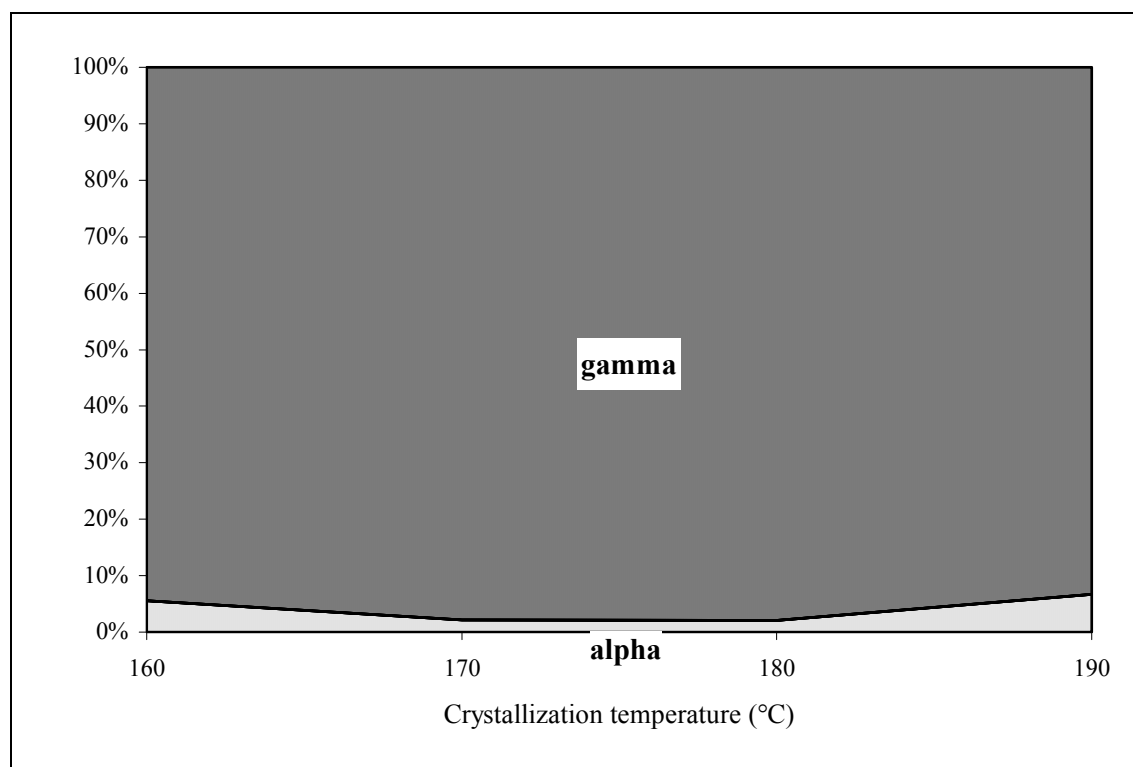


Fig.III. 23 Polymorphic composition in the neat iPP samples crystallized at different crystallization temperatures under 200 MPa pressure

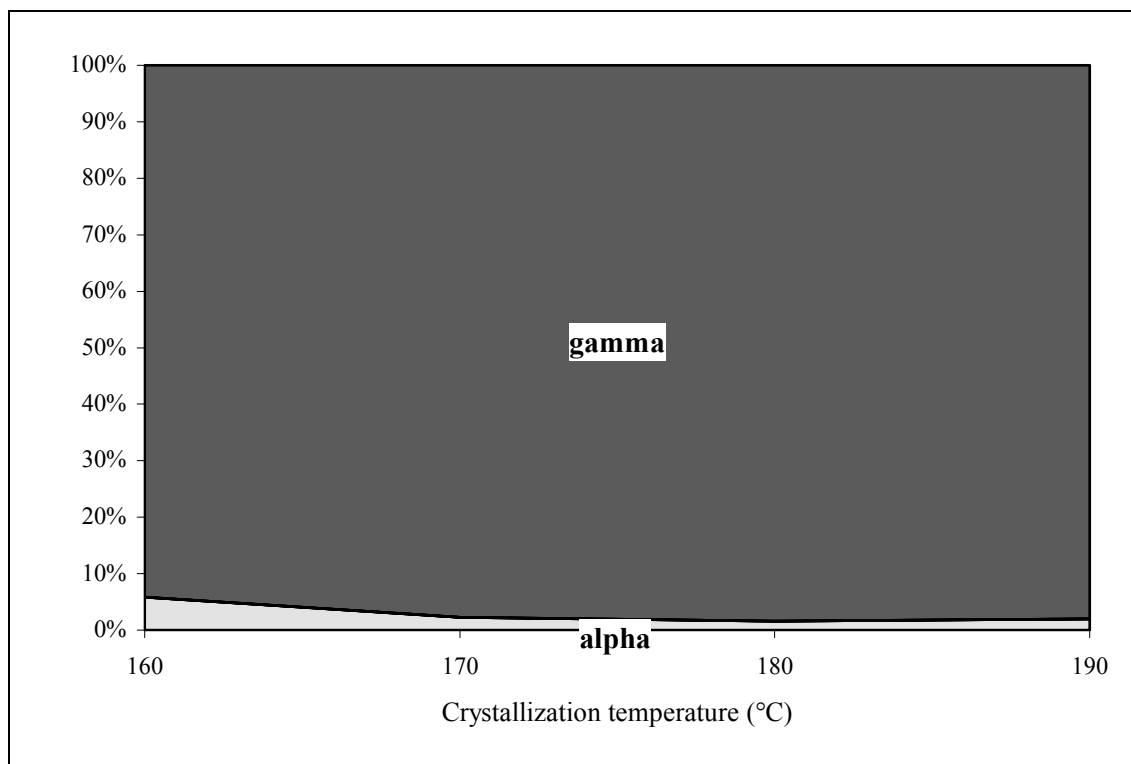


Fig.III. 24 Polymorphic composition in the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 200 MPa pressure

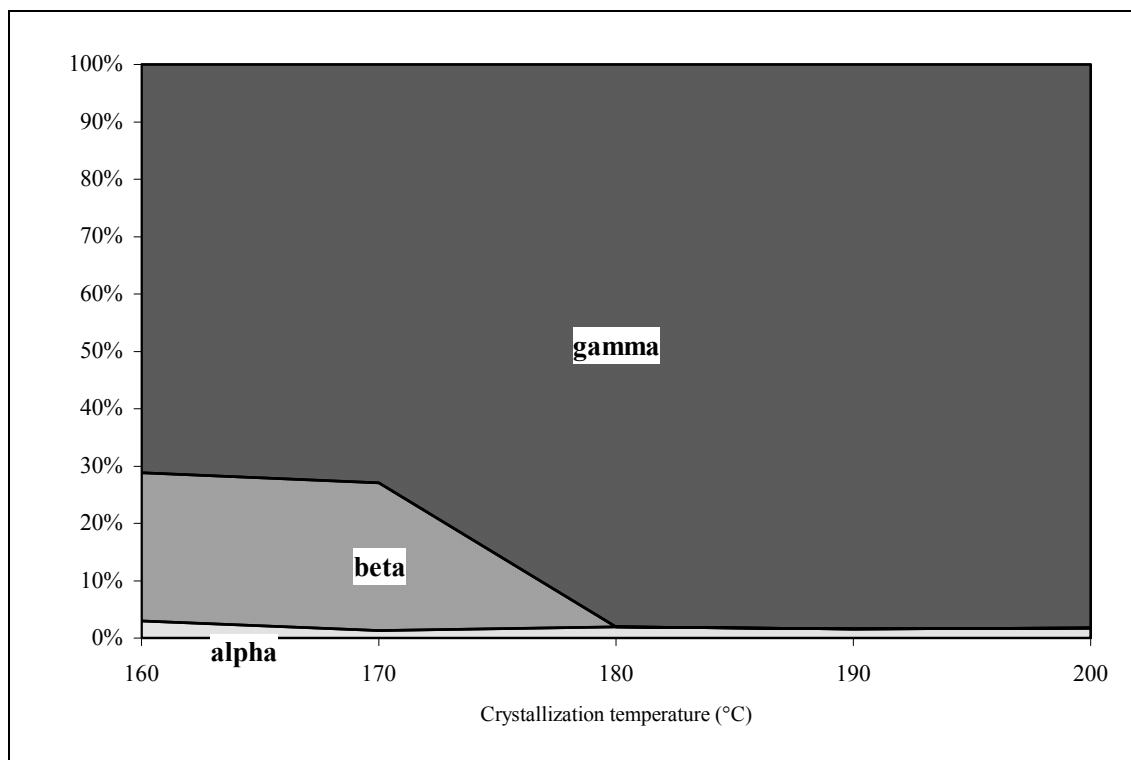


Fig.III. 25 Polymorphic composition in the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 200 MPa pressure

8.5 Non-isothermal, isobaric crystallization

The polymorphic composition in the samples non-isothermally crystallized under 100 MPa pressures was observed. The quantitative evaluation of WAXS data illustrated in *Fig.III. 26* and *Fig.III. 27* for neat iPP and samples with 0.01 wt.% NU100, respectively, shows practically identical polymorphic composition. It can be said that the effect of low amount of nucleant, in this case 0.01 wt.% NU100, is inhibited by 100 MPa pressure. However, it should be noted that the γ -phase content significantly decreases with rising cooling rate.

Fig.III. 28 presents the polymorphic composition of the samples with 0.03 wt.% NU100. It can be seen strong effect of the nucleator; in particular, at high cooling rates β -phase becomes predominant. The growth of β -phase is proceeding at the expense of α -phase at low cooling rates, while at high cooling rates β -phase suppresses both α - and γ -phases. In this case, the content of α -phase is very low and nearly β/γ crystalline system is obtained. Generally, in all cases illustrated in *Fig.III. 26*, *Fig.III. 27* and *Fig.III. 28* it can be seen the effect of high pressure and cooling rate; the predominant content of γ -phase (approx. 60 %) at low cooling rate virtually proportionally decreases with increasing rate.

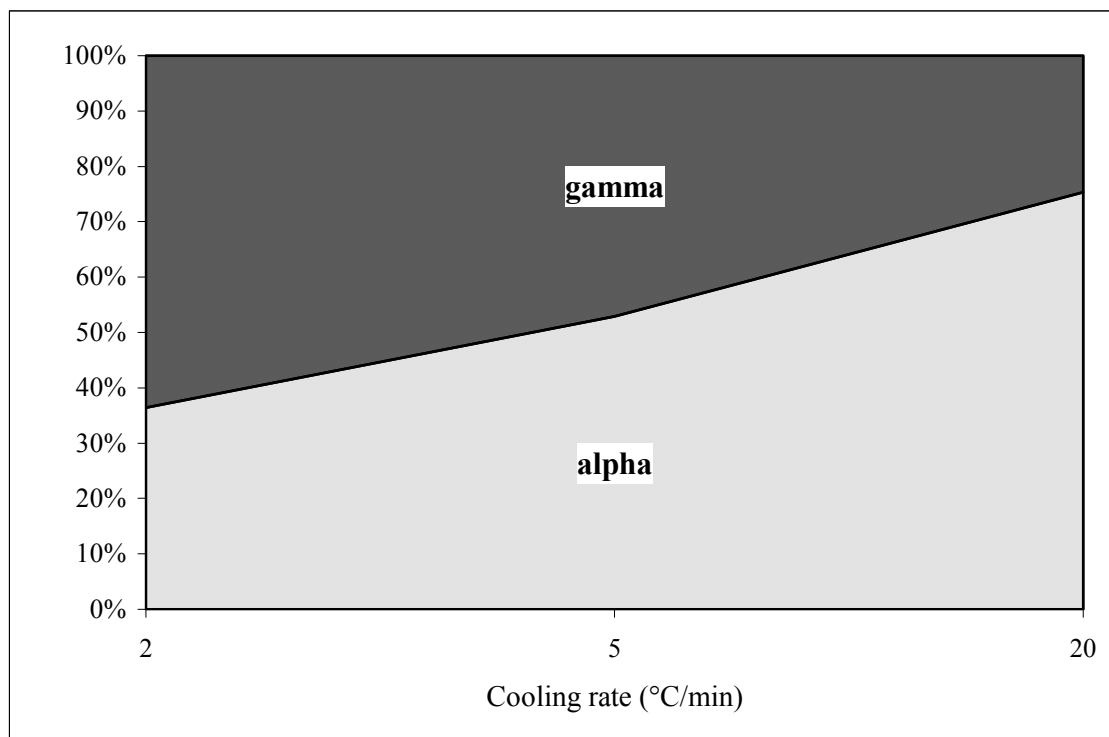


Fig.III. 26 Polymorphic composition in the neat iPP samples crystallized at different cooling rates under 100 MPa pressure

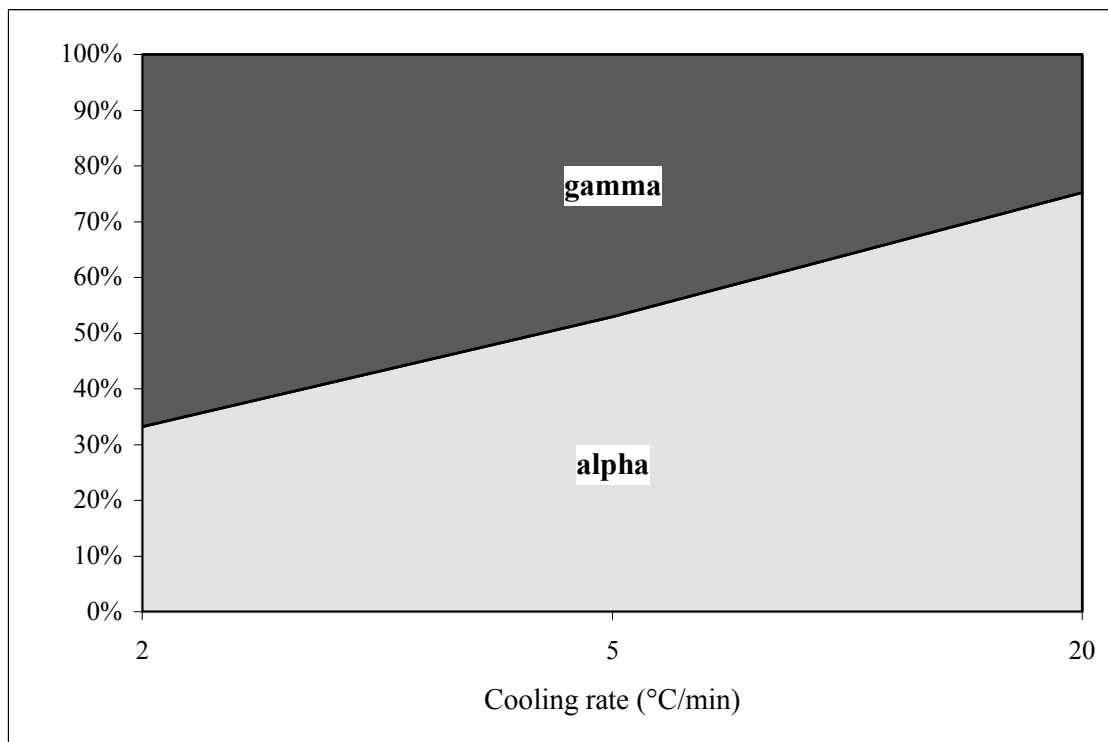


Fig.III. 27 Polymorphic composition in the samples containing 0.01 wt.% NU100 crystallized at different cooling rates under 100 MPa pressure

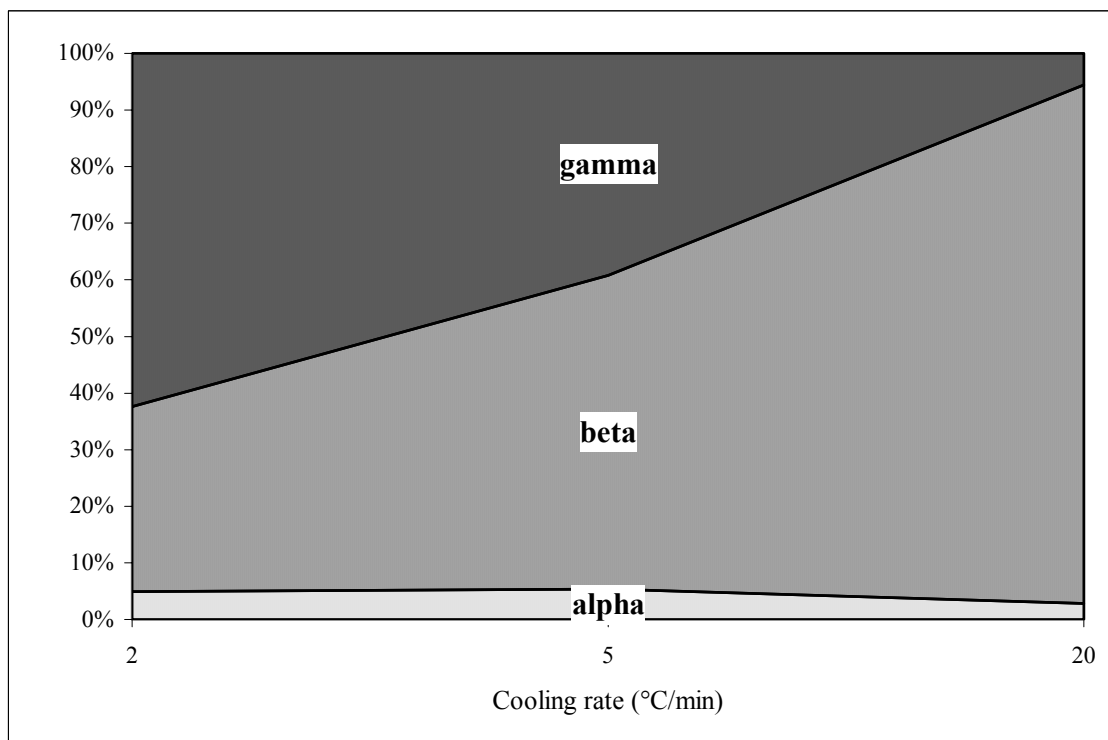


Fig.III. 28 Polymorphic composition in the samples containing 0.03 wt.% NU100 crystallized at different cooling rates under 100 MPa pressure

9 DSC ANALYSIS

To observe the melting behavior of high-pressure crystallized samples, differential scanning calorimetry was employed. Again, for purposes of discussion, the 100 MPa crystallization set was used.

Melting thermograms of neat and nucleated samples are illustrated in *Fig.III. 29*, *Fig.III. 30* and *Fig.III. 31*, in which the characteristic endothermic peaks of individual phases can be distinguished; the left peak approx. at 150°C was assigned to the melting of β -phase, middle approx. at 158°C to γ -phase and the right approx. at 165°C to α -phase. Indeed, there are the other smaller peaks and their interpretation has to be very careful, because the recrystallization process occurred during heating - one phase can melt and transform to the other one. In this case, the phase quantification from melting peaks is rather difficult, and generally, it does not correspond to the polymorphic structure quantification from the WAXS data. However, by the help of WAXS, the individual melting peaks can be unambiguously identified and assigned to a given crystalline phase.

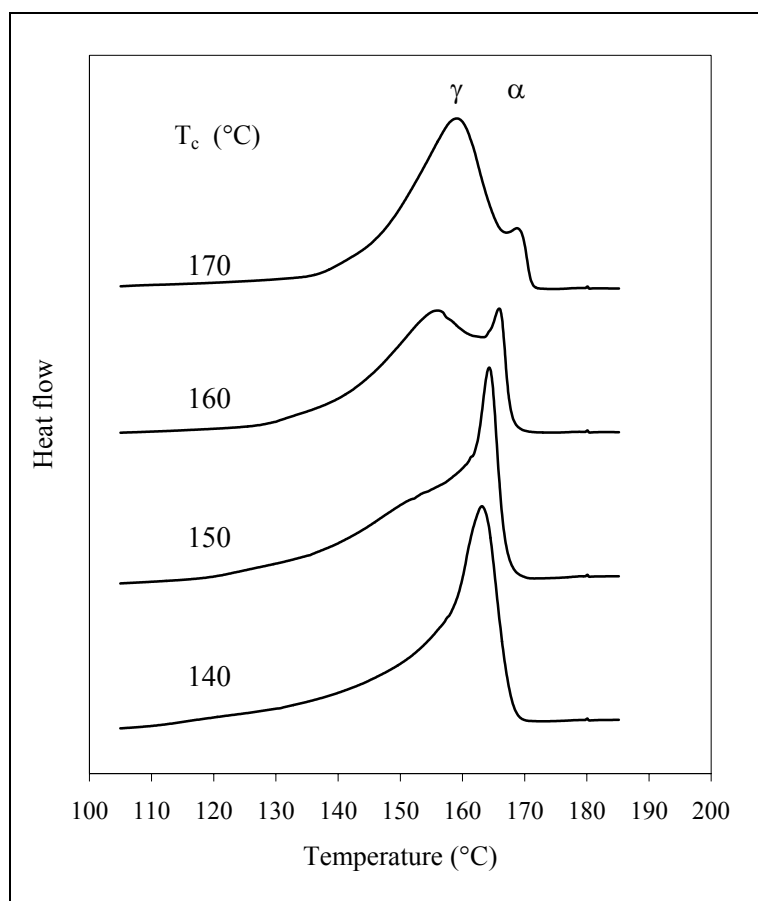


Fig.III. 29 Melting thermograms of the neat iPP samples crystallized at different crystallization temperatures under 100 MPa pressure

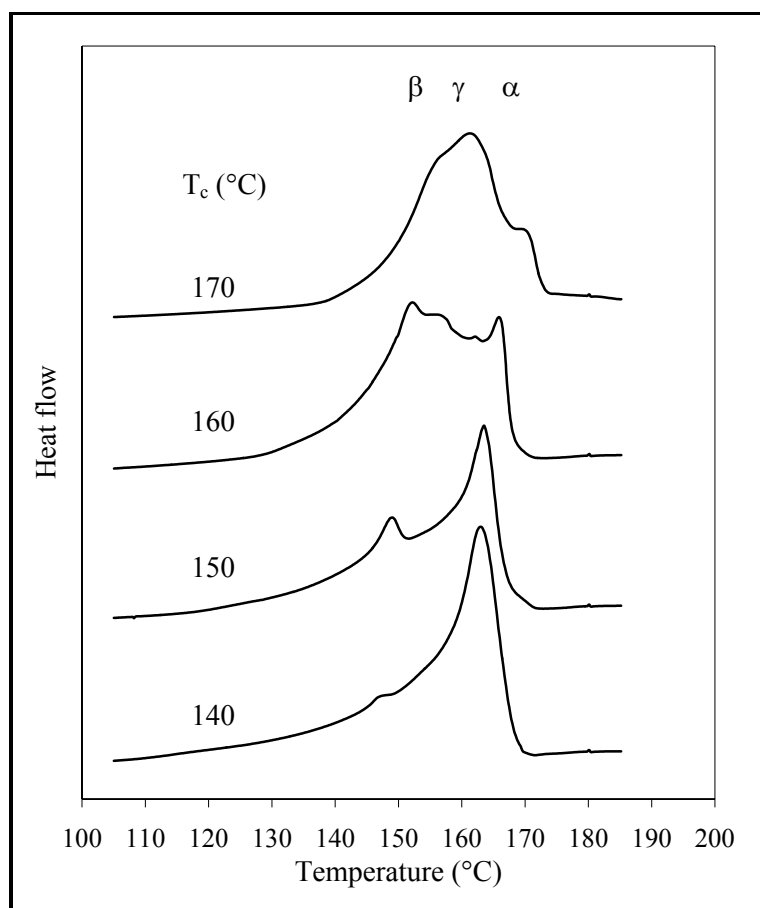


Fig.III. 30 Melting thermograms of the samples containing 0.01 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

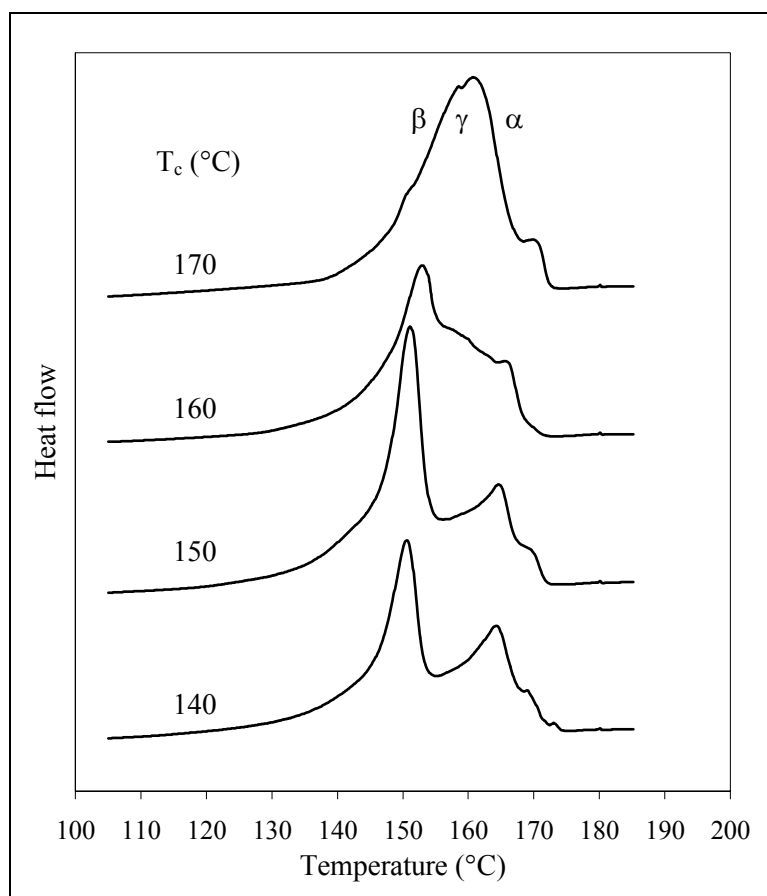


Fig.III. 31 Melting thermograms of the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under pressure 100 MPa

10 POLARIZED LIGHT MICROSCOPY

In detail, the morphology of the samples crystallized at 100 MPa are studied and shown in *Fig.III. 32*, *Fig.III. 33* and *Fig.III. 34*.

The morphology of the other samples prepared by high-pressure crystallization are summarized in Appendices – A 1.

In *Fig.III. 32*, the morphology of the neat iPP samples can be seen. It is known that both α - and γ - phases form spherulites typical by Maltese crosses under polarized light. When the γ -phase content is rather low the spherulites of both crystal phases occupy the same spherulites; however, with increasing γ -phase content the γ -spherulites possesses a quite different appearance – they form a feather-like structure [31]. In this context, the morphology of multi-component crystalline systems has to be discussed with help of WAXS measurements. At $T_c = 170^\circ\text{C}$ and 160°C , the γ -phase is predominant and the spherulites of γ -phase with its typical feather-like structure are actually observed. This peculiar morphology is also clearly evident in Ap. A I. 5. At crystallization temperature $T_c = 150^\circ\text{C}$, a different kind of spherulitic morphology with mixed α - and γ - spherulites was obtained. Similar situation can be seen at $T_c = 140^\circ\text{C}$; large α -spherulites and around them smaller γ - spherulites can be observed; it should be noted that this sample consisted of the same content of α - and γ - phases.

Generally, the effect of increasing crystallization temperature on the spherulite size is rather low.

Photographs in *Fig.III. 33* show the morphology of nucleated iPP containing 0.01 wt.% NU100. Photograph ($T_c = 170^\circ\text{C}$) shows the morphology with 75 % amount of γ -phase, 20 % of β -phase and insignificant 5 % of α -phase. The γ -spherulites with distinct Maltese crosses are overgrown by fine-grained fields of β -phase morphology. Abstractedly, the morphology possesses a carpet-like appearance – a matrix indicating by β -morphology is decorated by ornaments rising from γ -spherulites. This morphology is particularly evident in Ap. A I. 2.

Photograph ($T_c = 160^\circ\text{C}$) shows the morphology with 70 % of γ -phase, 20 % of β -phase and 10 % of α -phase. Compared with previous morphology, significant morphological changes occur. The spherulites typical for each crystalline phase can be

observed – α -spherulite with distinct Maltese crosses, feather-like γ -spherulites and β -structures without evident Maltese crosses. Similar morphologies can be found at crystallization temperatures 150 and 140°C. In the case of the sample with 0.01 wt.% NU100, the spherulite size evidently increased with rising T_c .

Fig.III. 34 presents the morphology of the sample containing 0.03 wt.% NU100. The heterogeneous nucleation causes a generation of high number of nuclei and that is why the morphology is fine-grained. Therefore, it is difficult to assign the spherulites to a given crystalline phase. In all samples of this set, the content of α -phase is very low, approx. 5 %. The samples crystallized at $T_c = 150^\circ\text{C}$ and 140°C possesses almost the same polymorphic composition - more than 50 % of β -phase and approx. 40 % of γ -phase. The sample crystallized at 160°C contains approx. 57 % of γ -phase and 40 % of β -phase. However, the morphology of mentioned specimens is virtually similar, i.e. they have a similar spherulite size. Actually, in this case the β -nucleant can be taken as general heterogeneous nuclei for both γ - and β - phases.

The crystalline phase of the sample crystallized at $T_c = 170^\circ\text{C}$ contains 83 % of γ -phase and 12 % of β -phase. What can be surprisingly seen is a slight increase of spherulite size as compared to previous samples (compare also *A I. 3* and *A I. 9*). This exemplifies the strong effect of high pressure (synergy applied with high temperature) on crystallization of polypropylene.

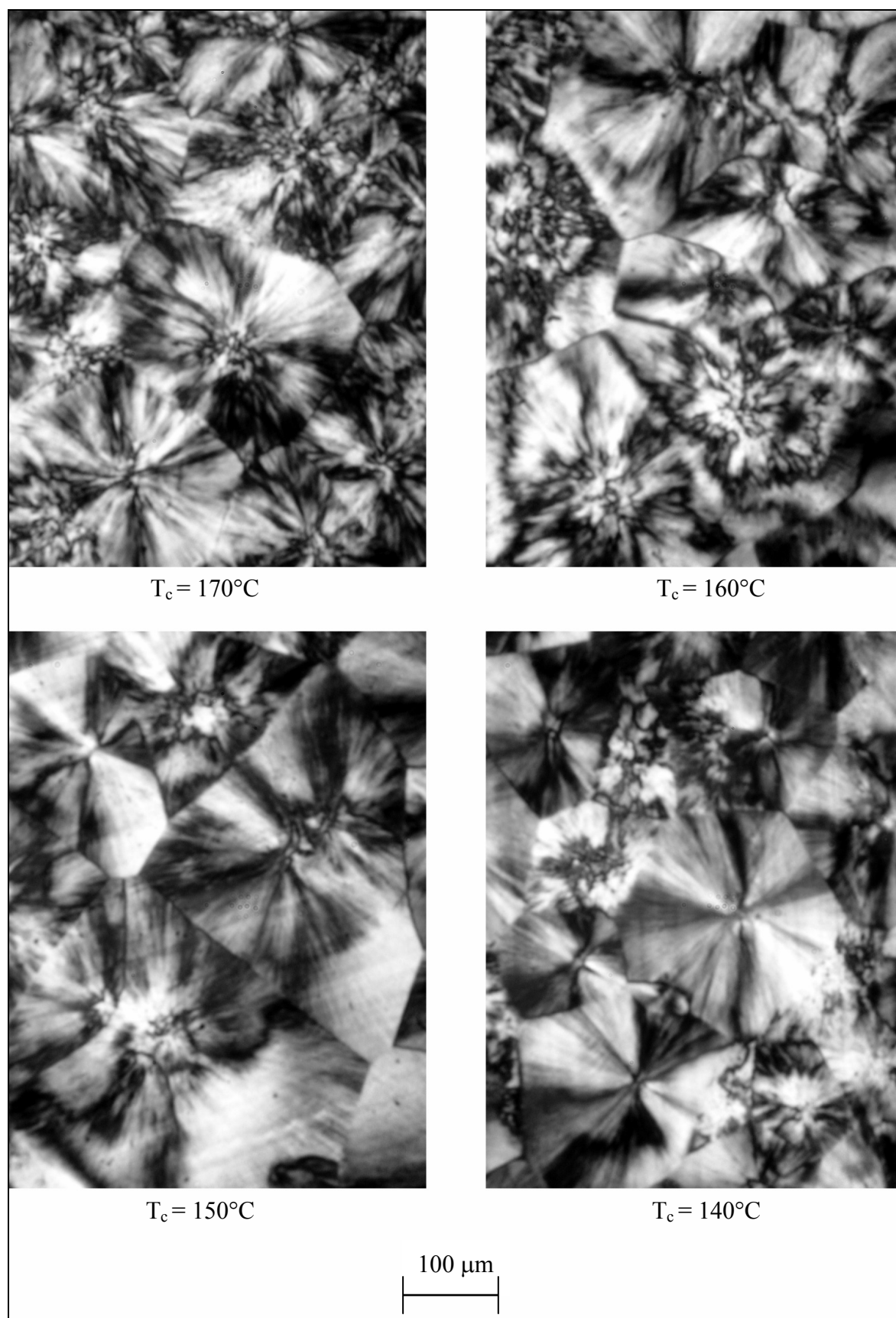


Fig.III. 32 Morphology of the neat iPP samples crystallized at different crystallization temperatures under 100 MPa pressure

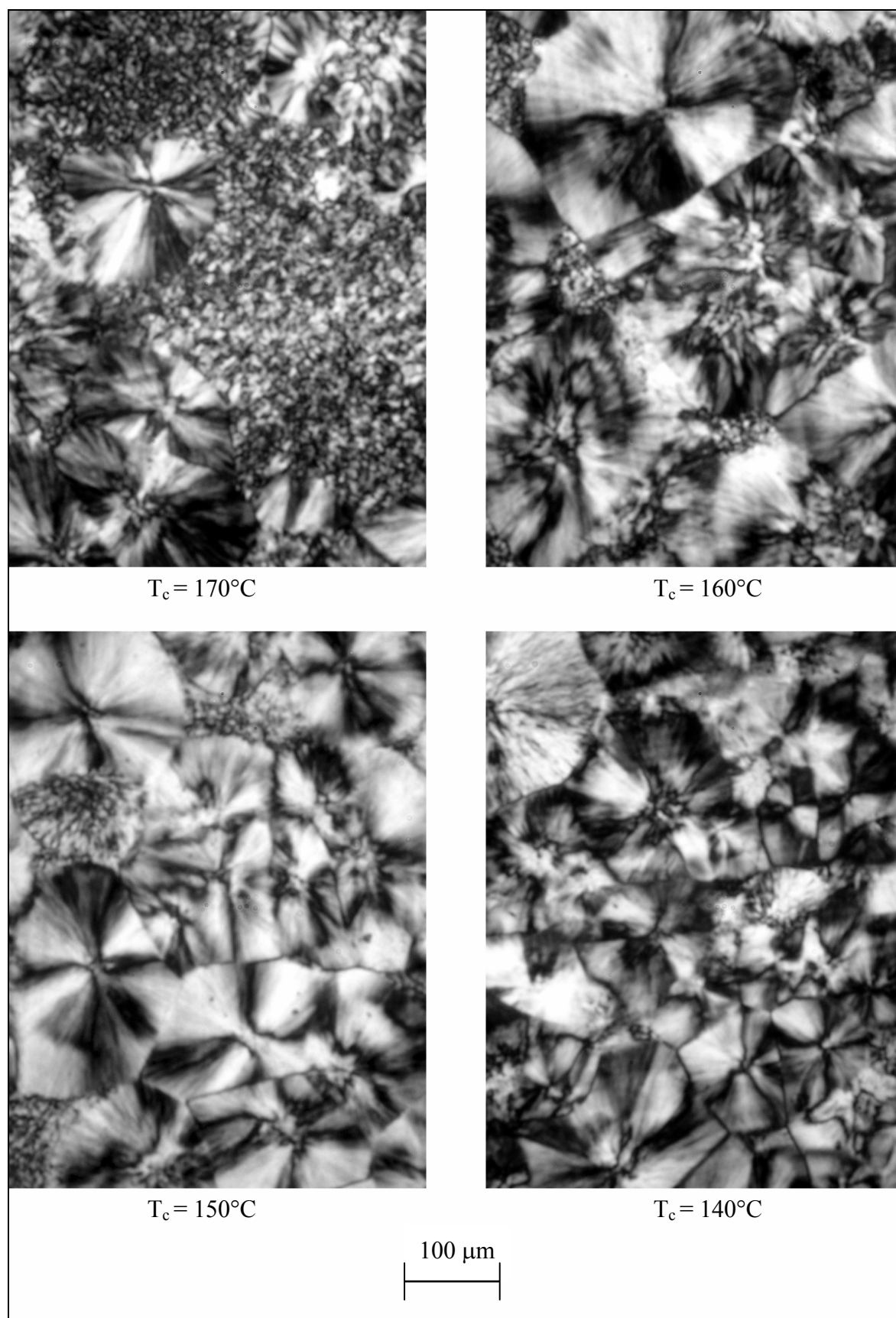


Fig.III. 33 Morphology of the samples containing 0.01 wt.% NUI100 crystallized at different crystallization temperatures under 100 MPa pressure

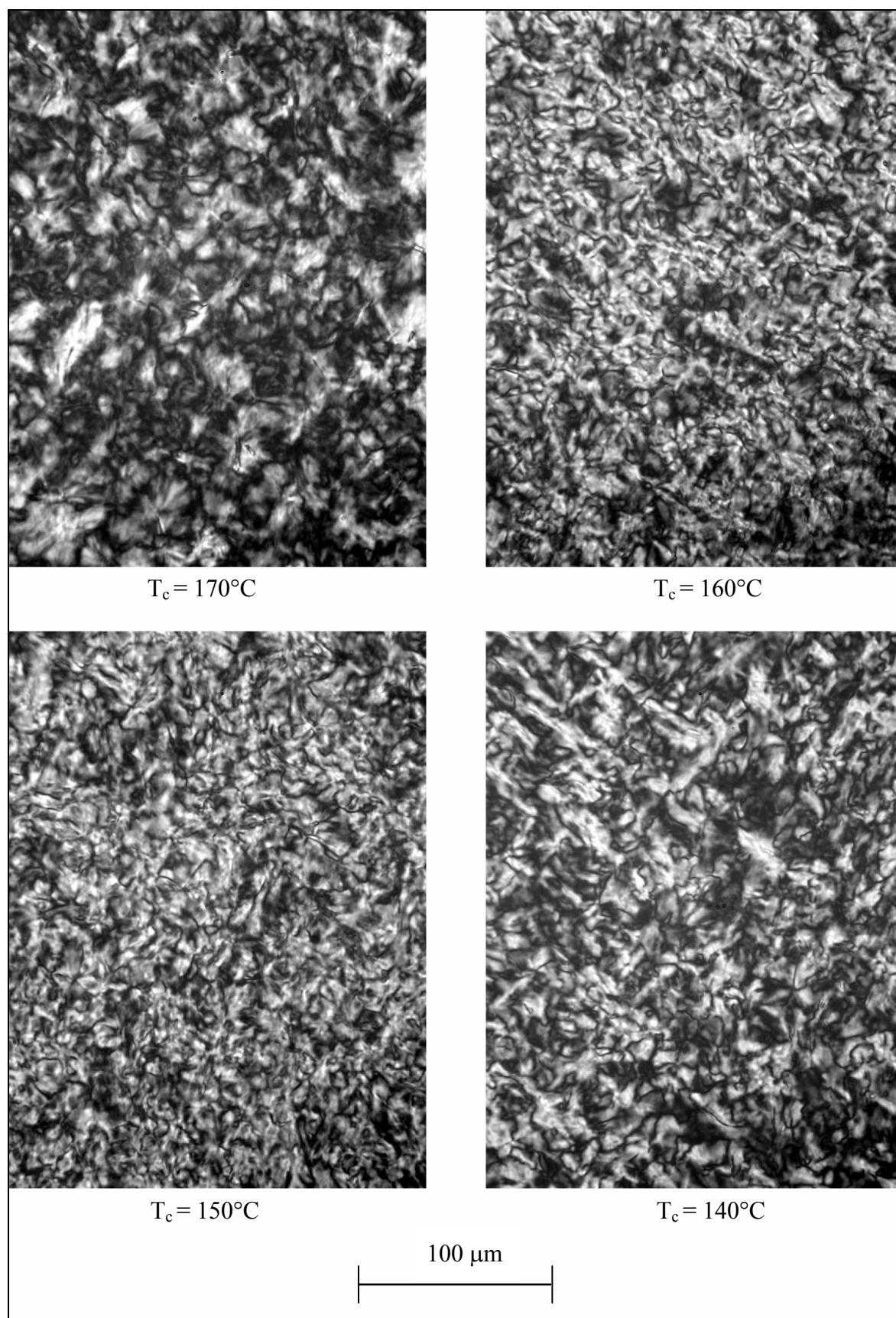


Fig.III. 34 Morphology of the samples containing 0.03 wt.% NU100 crystallized at different crystallization temperatures under 100 MPa pressure

11 DYNAMIC-MECHANICAL THERMAL ANALYSIS

Samples isothermally crystallized under 100 MPa pressure and for comparing 3 other samples containing the highest volume of α -, β - and γ - phases were analyzed by DMTA.

Fig.III. 35 shows the effect of crystallization temperature on storage modulus E' . There is not a significant dependence and only slightly increasing trend of modulus can be observed. The situation is complicated by varying polymorphic composition and improvement of morphology with rising T_c . It should be also noted that the measurement could be slightly influenced by the character of specimens, the size of which was critical for DTMA measurements.

What is particularly important, are three lines of nearly pure α -, β - and γ - phases, respectively, indicating the storage modulus of individual crystalline phases. It is evident that the lowest modulus is associated with practically pure β -phase, while the modulus of pure α - and γ - phase is higher as compared to β -phase and mutually comparable. These results are confirmed by values of loss angle (see *Fig.III. 36*)

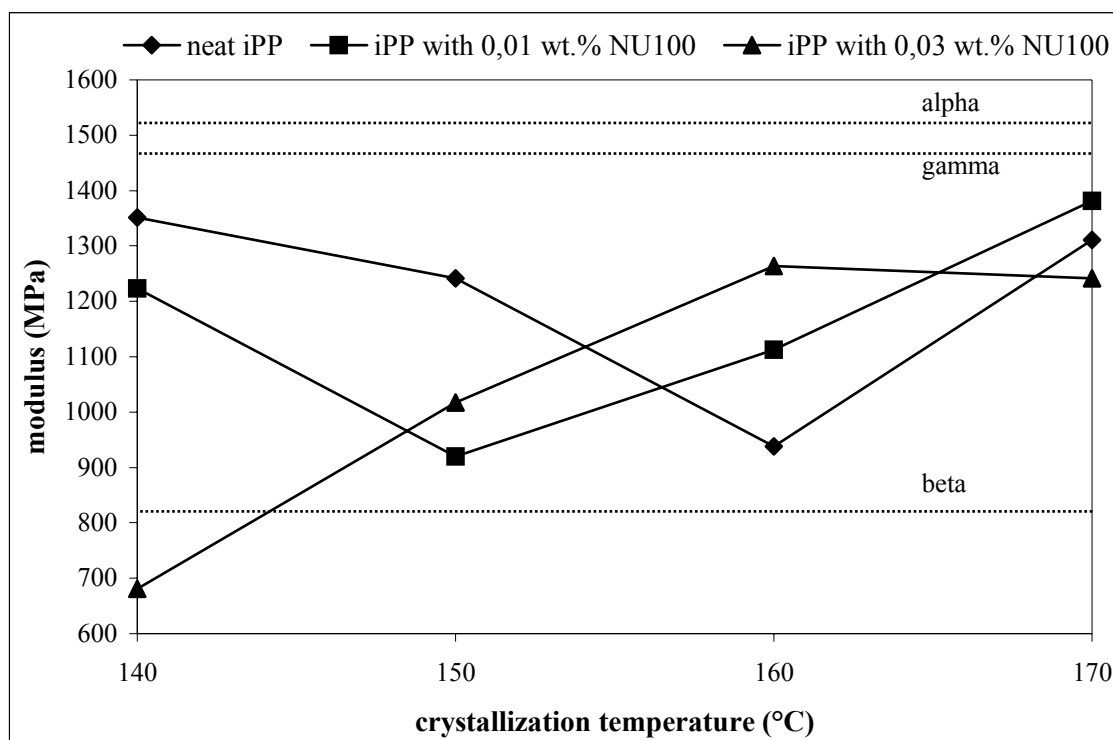


Fig.III. 35 Dependence of storage modulus on crystallization temperature of isothermally crystallized samples under 100 MPa pressure

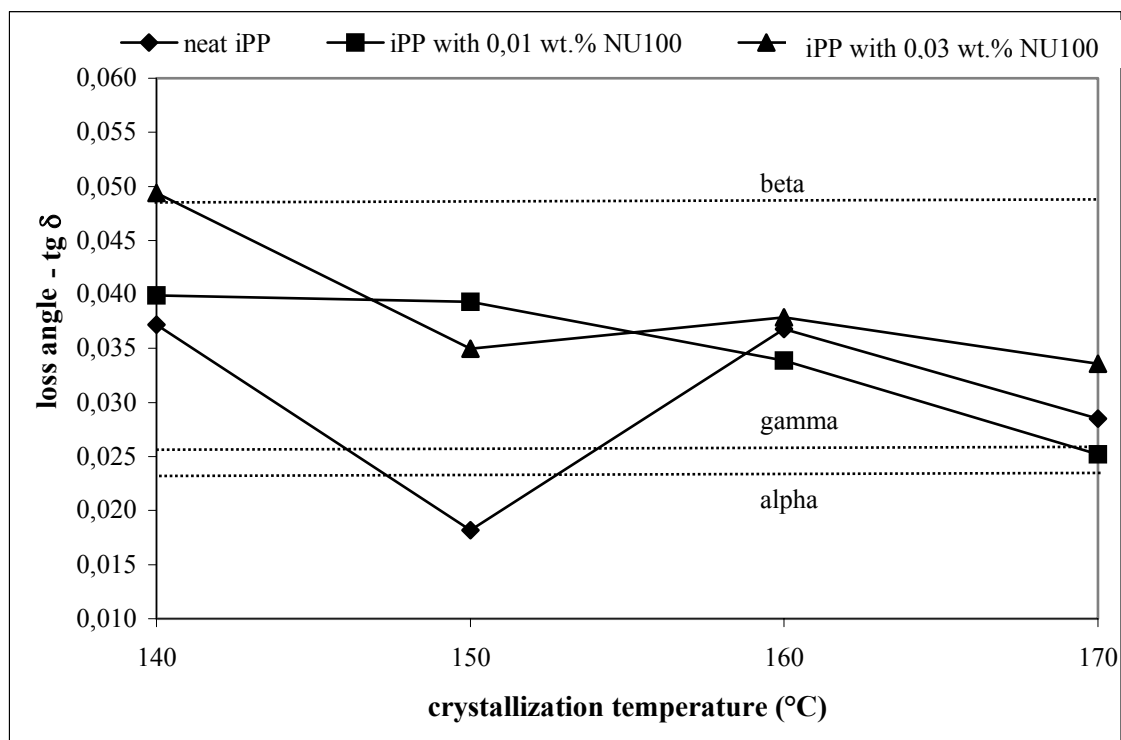


Fig.III. 36 Dependence of loss angle, $\text{tg } \delta$, on crystallization temperature of isothermally crystallized samples under 100 MPa pressure

12 SHORE D MEASUREMENT

The Shore D measurements were carried out on samples isothermally crystallized under 100 MPa pressure, and for comparison 3 other samples containing the highest contents of α -, β - and γ - phase, respectively. The results are illustrated in *Fig.III. 37*.

There can be seen that increasing crystallization temperature caused the increase of hardness, particularly reflecting structural improvement. This also complicates an explanation of hardness changes by polymorphic variation. What can be seen from the hardness comparison of nearly pure morphological structures is: γ -phase possesses the highest hardness and β -phase, on the contrary, the lowest hardness. The α -phase hardness is in the middle of the γ - β range.

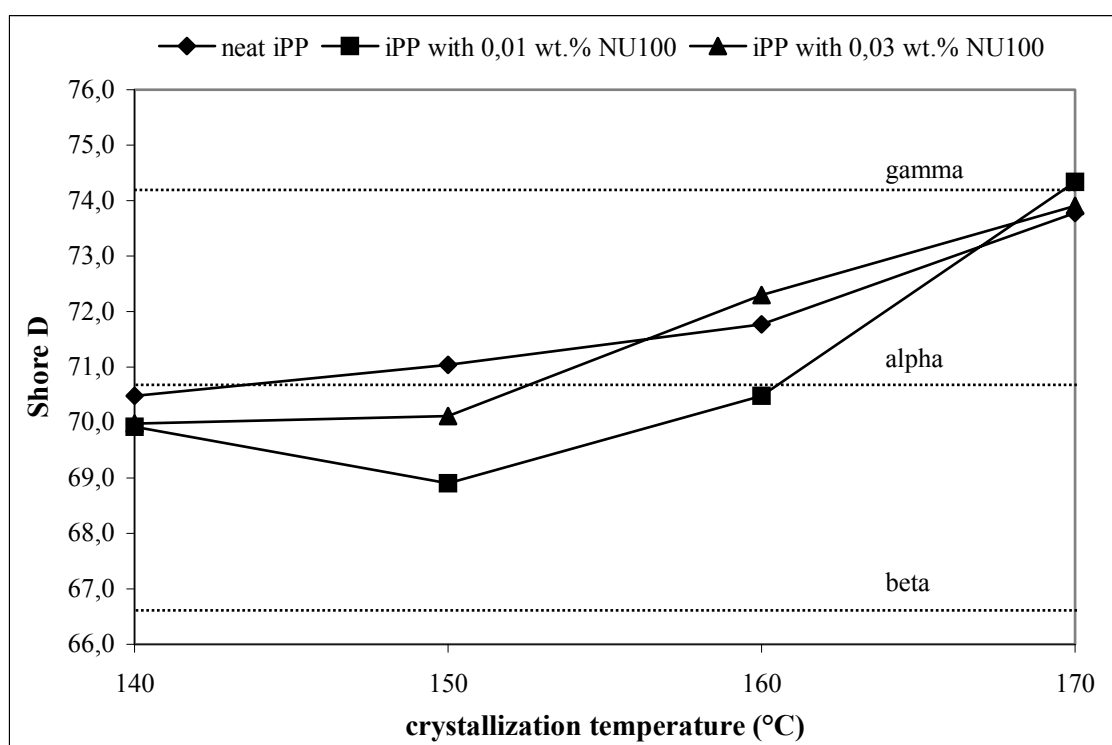


Fig.III. 37 Dependence of Shore D hardness on crystallization temperature of isothermally crystallized samples under 100 MPa pressure

CONCLUSIONS

This master thesis deals with a study of novel method for the preparation of unique three-phase crystalline systems in isotactic polypropylene; the method is based on a synergy application of a specific β -nucleating agent and high pressure during crystallization.

Isothermal crystallization kinetics of nucleated iPP under low (50 MPa) pressure show much shorter crystallization times and K values compared to neat iPP, the increase of crystallization pressure (100, 150 and 200 MPa) inhibited the effect of low amount of NU100, and crystallization kinetics of nucleated samples was approaching to the neat iPP. Interpretation of exponent n should be very careful, because its values are between 0.7 - 2.0, which did not exactly correspond with the Avrami theory.

Non-isothermal crystallization proves the theory of decreasing crystallization temperature with increasing cooling rate. Crystallization temperatures of the samples containing 0.01 wt.% NU100 were higher as compared to neat samples. In the neat iPP samples could be seen linear increase of amount of α -phase with rising cooling rate at the expense of γ -phase. Strong effect of nucleant in the samples with 0.03 wt.% NU100 could be seen at high cooling rates; consequently β -phase becomes predominant.

WAXS provided the quantification of polymorphic composition in all samples. In conditions of isothermal crystallization, in all cases except the set with 50 MPa samples, the amount of γ -phase increases with rising crystallization temperature and pressure, at the highest pressures and temperatures γ -phase became predominant.

The amount of β -phase in the samples crystallized at 150 and 200 MPa rapidly decreases with rising temperature, and in the highest temperature β -phase disappeared on the expense of γ -phase. At high pressures, the effect of 0.01 wt.% nucleant was totally inhibited; its effect could be seen only in the samples crystallized at 50 and 100 MPa.

In the neat iPP samples, the amount of α -phase decreases to insignificant amount with rising crystallization temperature and pressure, except the samples crystallized at 50 MPa.

A study of melting behavior was performed only on the samples isothermally crystallized under 100 MPa pressure. There can be observed characteristic melting peaks

for each crystalline form; in nucleated samples the additional recrystallization peaks could be detected.

Polarized light microscopy provided interesting insight into the morphology of all samples. High crystallization temperatures allowed the formation of spherulites with large dimension, in particular in the sample with 0.01 wt.% NU100. Heterogeneous nucleation significantly decreased the spherulite size. The characteristic structures for each crystalline phase were observed.

Mechanical properties of the samples isothermally crystallized under 100 MPa pressure showed the positive effect of increased crystallization temperature on hardness and modulus. DMTA showed complicated mechanical behavior of polymorphic crystalline systems, the interpretation of which should be particularly careful. While β -phase possessed lower modulus as compared to common α -phase, the modulus of γ -phase is virtually comparable with α -phase.

Finally, it can be noted that this work offers detailed characterization of high-pressure crystallization of nucleated isotactic polypropylene. As a result, multi-component crystalline structures are obtained. It should be noted that the number of physical properties of β/γ and $\alpha/\beta/\gamma$ crystalline systems have not been reported yet, particularly due to a complicated preparation of representative samples. The multi-scale approach described in this work could be thus a way for further investigation of polymorphism of iPP.

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LIST OF SYMBOLS AND SHORTCUTS

iPP		isotactic polypropylene
α		monoclinic crystallic phase of polypropylene
β		trigonal crystallic phase of polypropylene
γ		orthorhombic crystallic phase of polypropylene
pVT		pressure-volume-temperature
DSC		differential scanning calorimetry
WAXS		wide angle X-ray scattering
DMTA		dynamic-mechanical thermal analysis
TG		thermogravimetry
TMA		thermomechanical analysis
PLM		polarized light microscopy
ΔG	(J)	Gibbs free energy
ΔH	(J)	enthalpy
ΔS		entropy
T	(°C)	temperature
T_m	(°C)	melting temperature
T_c	(°C)	crystallization temperature
T_g	(°C)	glass transition temperature
t	(min)	time
$t_{0,5}$	(min)	halftime of primary crystallization
θ	(%)	relative proportion of crystallized material
θ_n	(%)	relative proportion of non-crystallized material
K or Z	(s ⁻ⁿ)	constant of nucleation from Avrami equation
n		constant of growth from Avrami equation
X_t		volume fraction of crystalline material
wt. %	(%)	weight percent
λ	(nm)	wavelength
2θ	(°)	angle of diffraction
d	(nm)	interplanar distance
Δc_p	(J)	heat capacity
v	(cm ³ .g ⁻¹)	specific volume
M_n, M_w	(g.mol ⁻¹)	molecular weight
p	(MPa)	pressure
$h_{\alpha 1}$		intensity of α -diffraction peak corresponding to angle $2\theta = 14.2^\circ$
$h_{\alpha 2}$		intensity of α -diffraction peak corresponding to angle $2\theta = 17.0^\circ$
$h_{\alpha 3}$		intensity of α -diffraction peak corresponding to angle $2\theta = 18.8^\circ$
h_β		intensity of β -diffraction peak corresponding to angle $2\theta = 16.2^\circ$
h_γ		intensity of γ -diffraction peak corresponding to angle $2\theta = 19.9^\circ$
G'		dynamic storage modulus
G''		dynamic loss modulus
tg δ		loss angle

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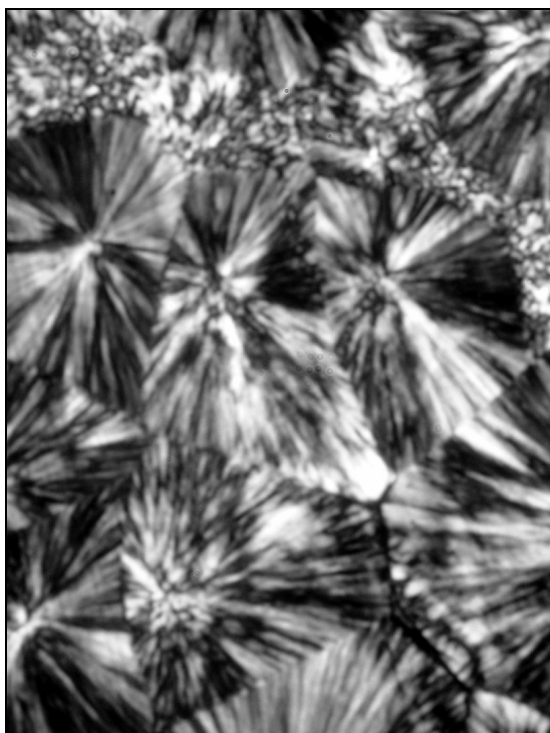
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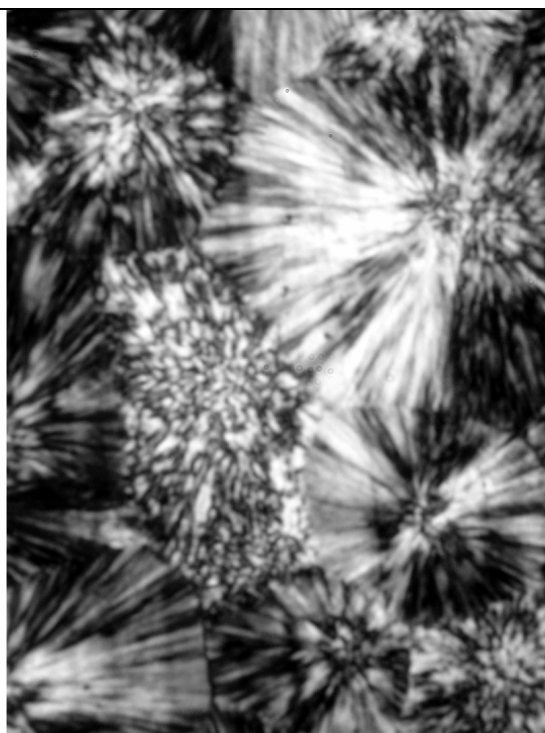
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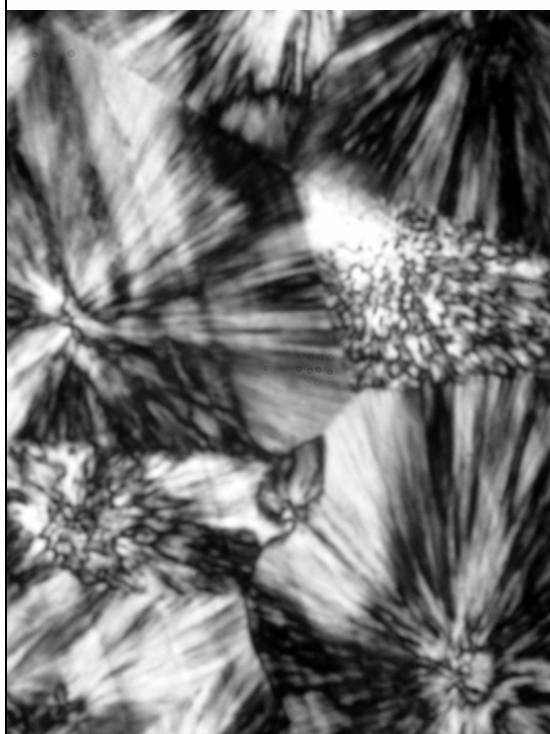
A 1: MORPHOLOGY OF ALL PREPARED SAMPLES



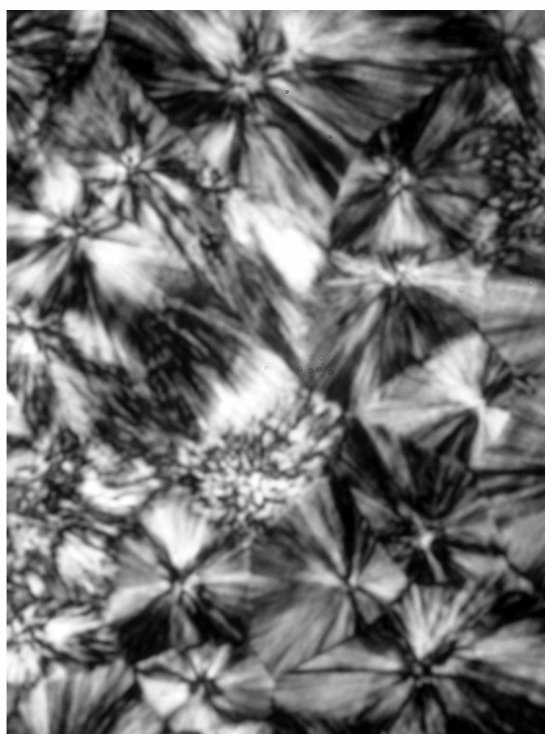
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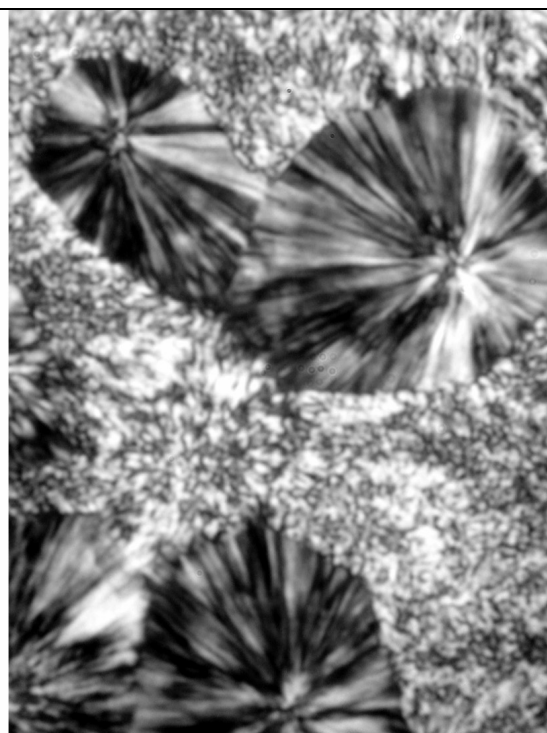
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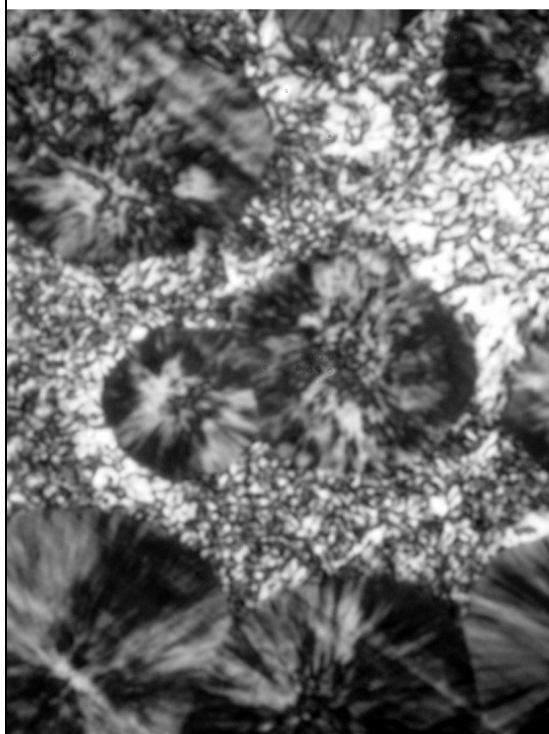
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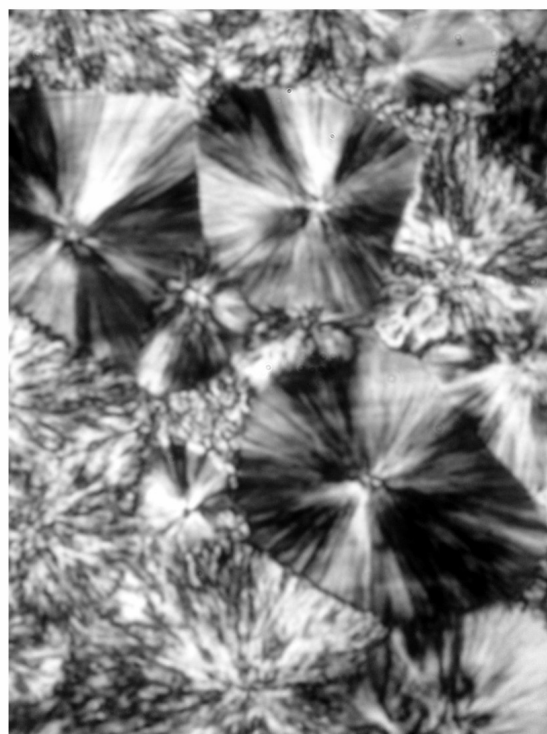
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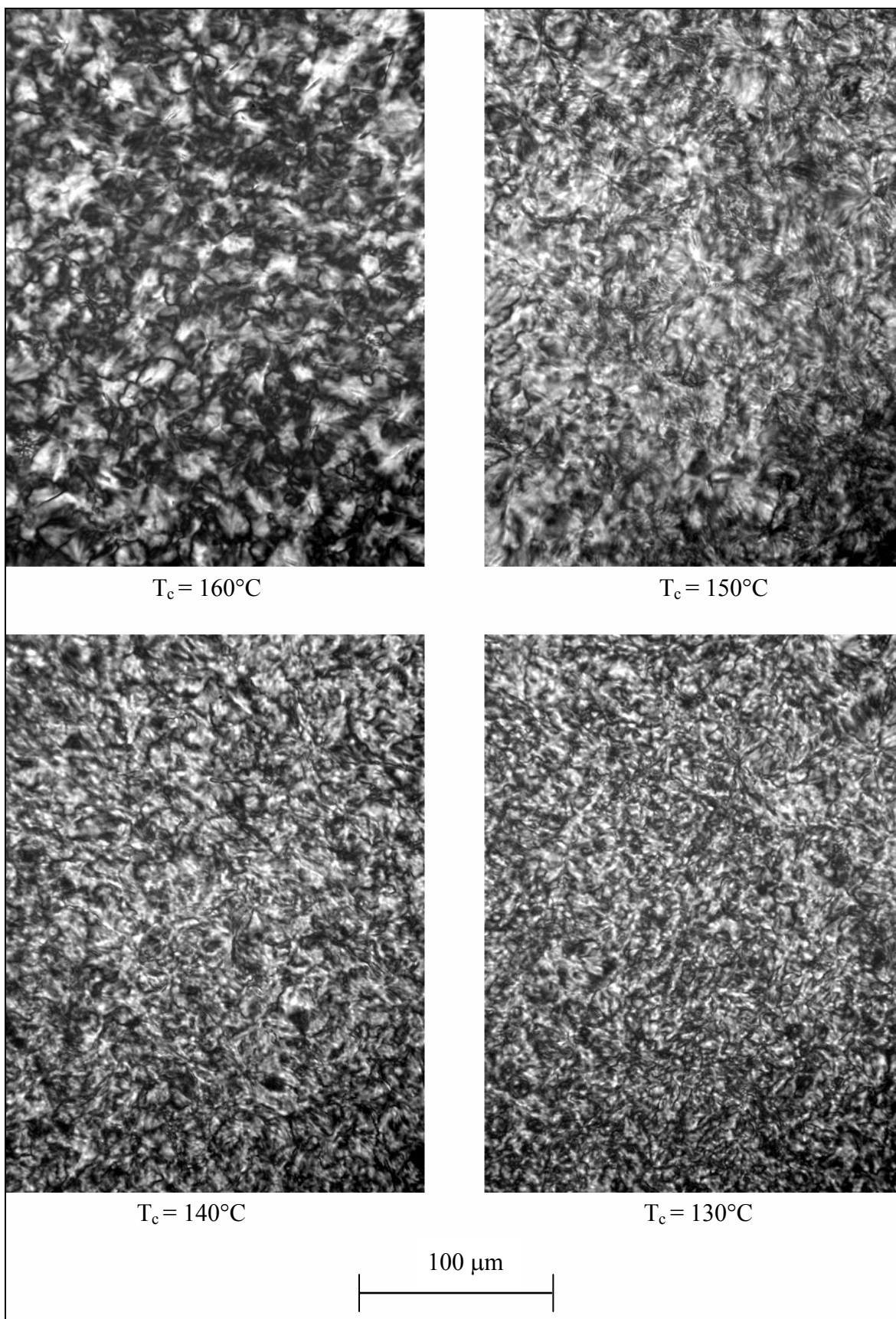
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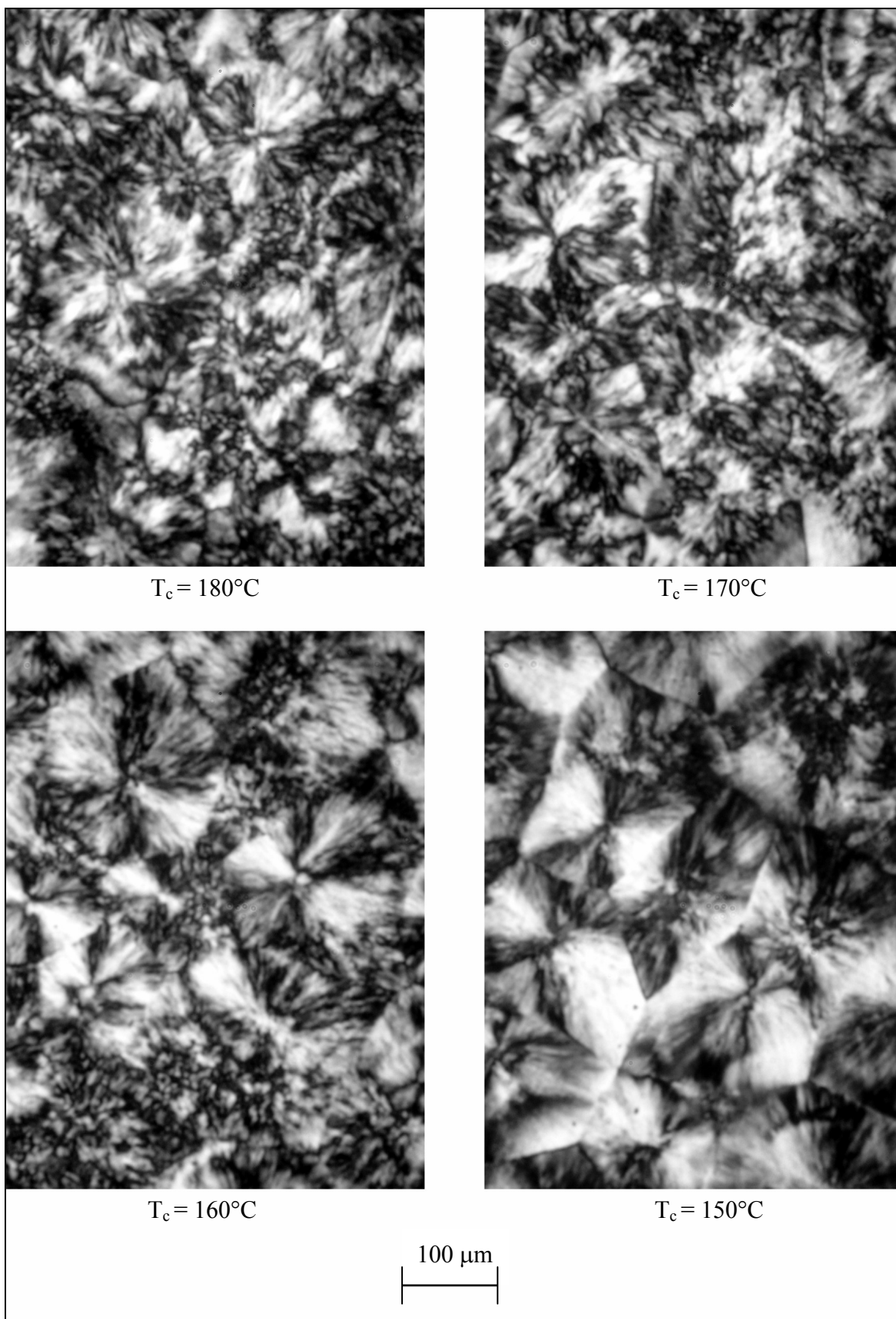
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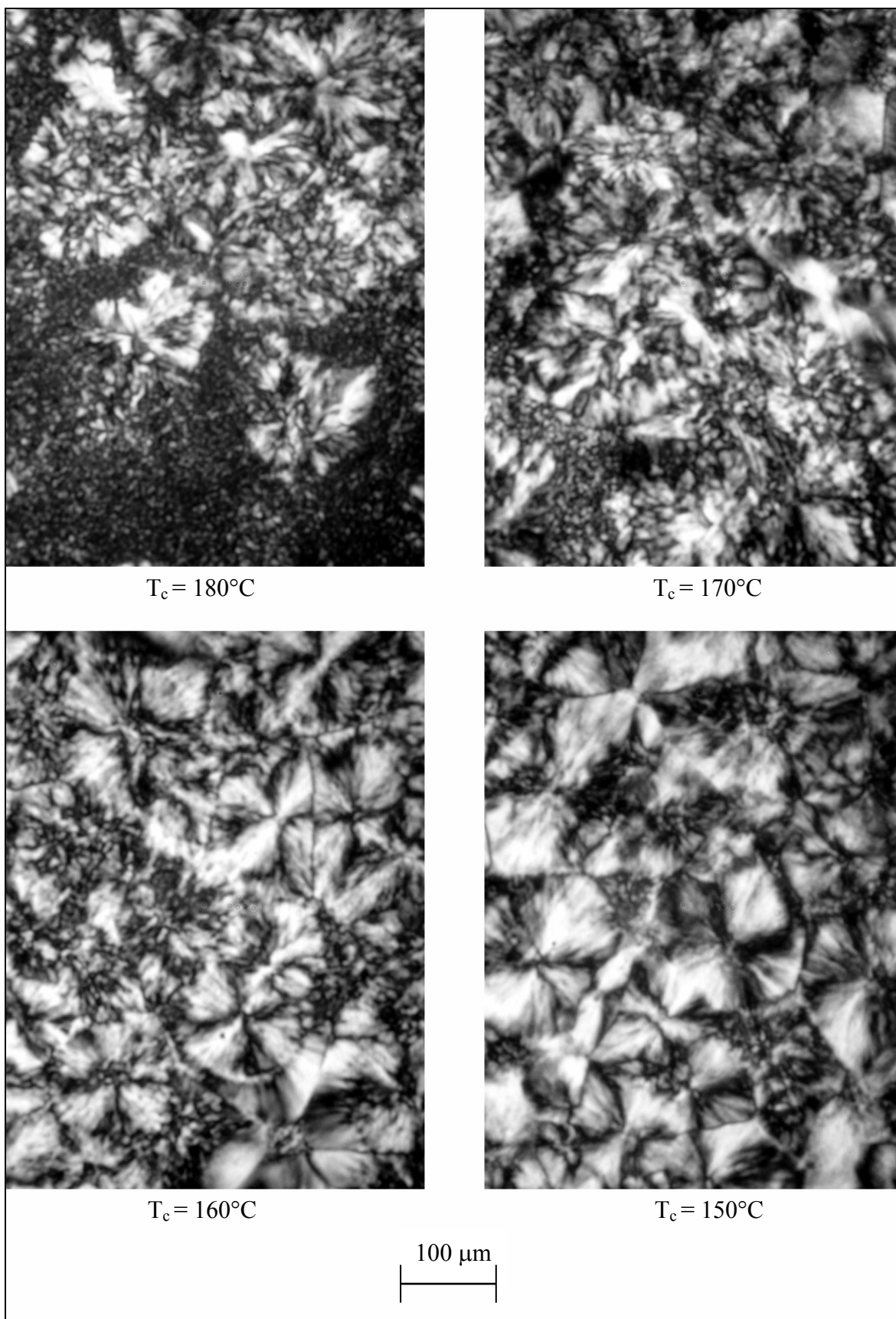
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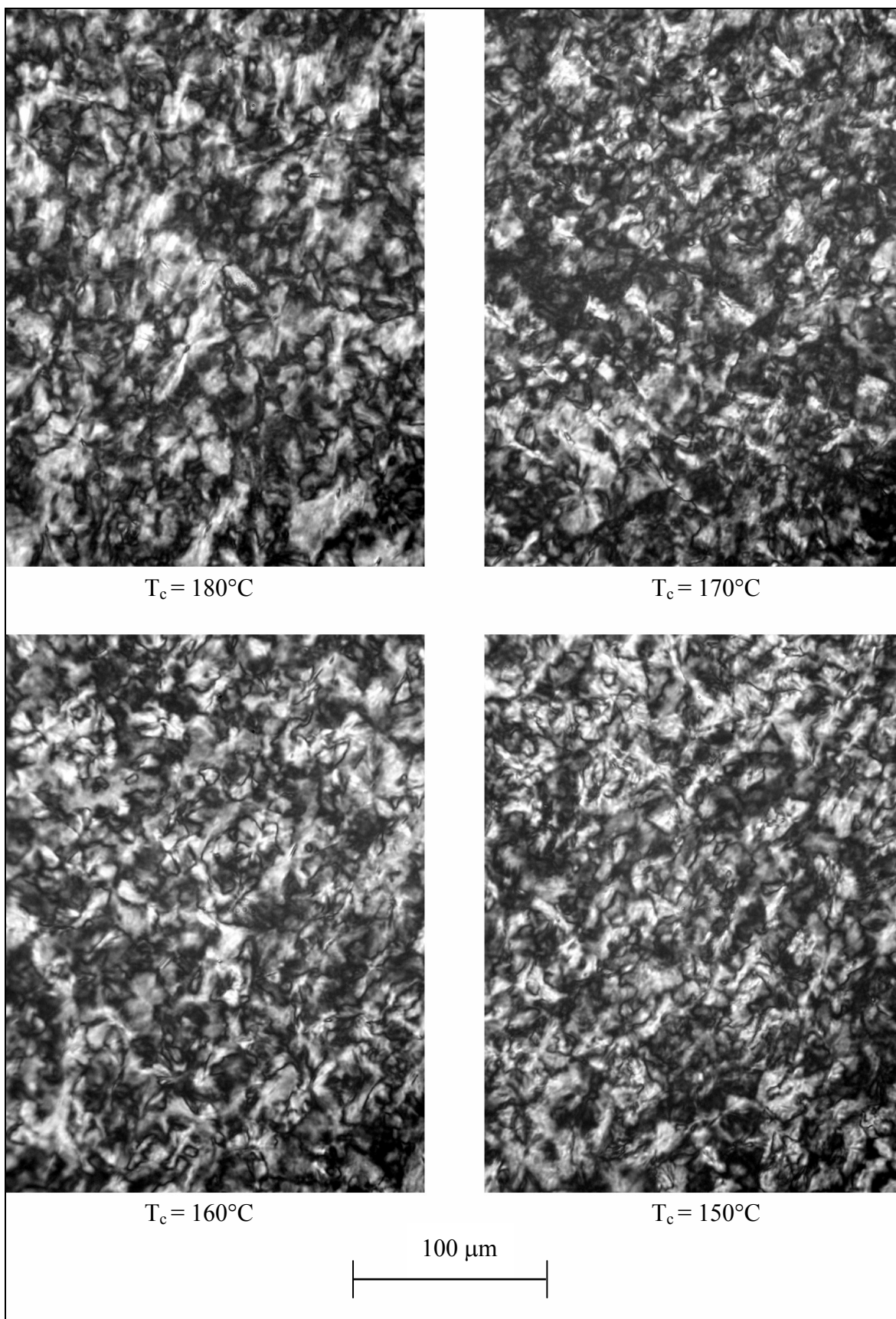
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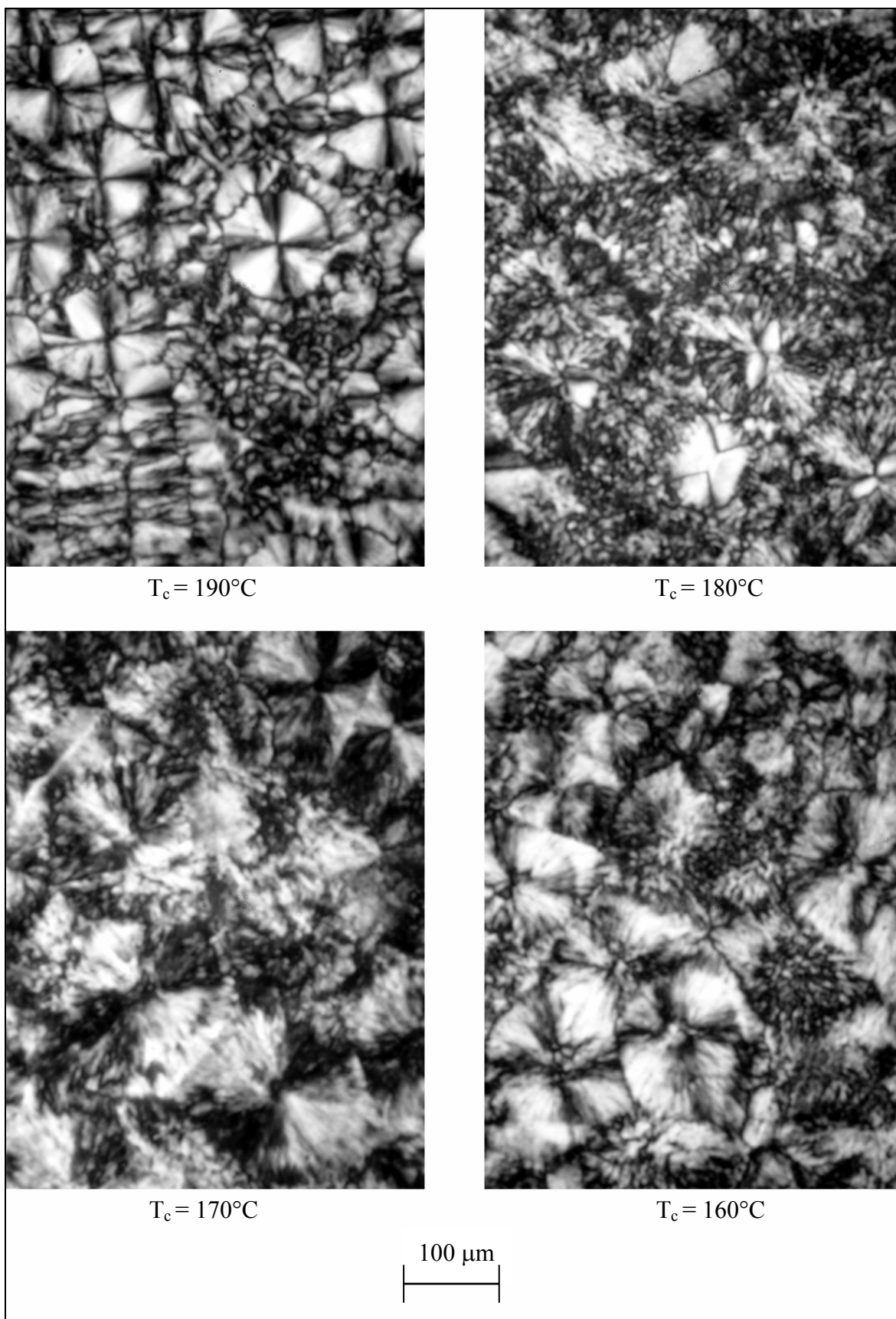
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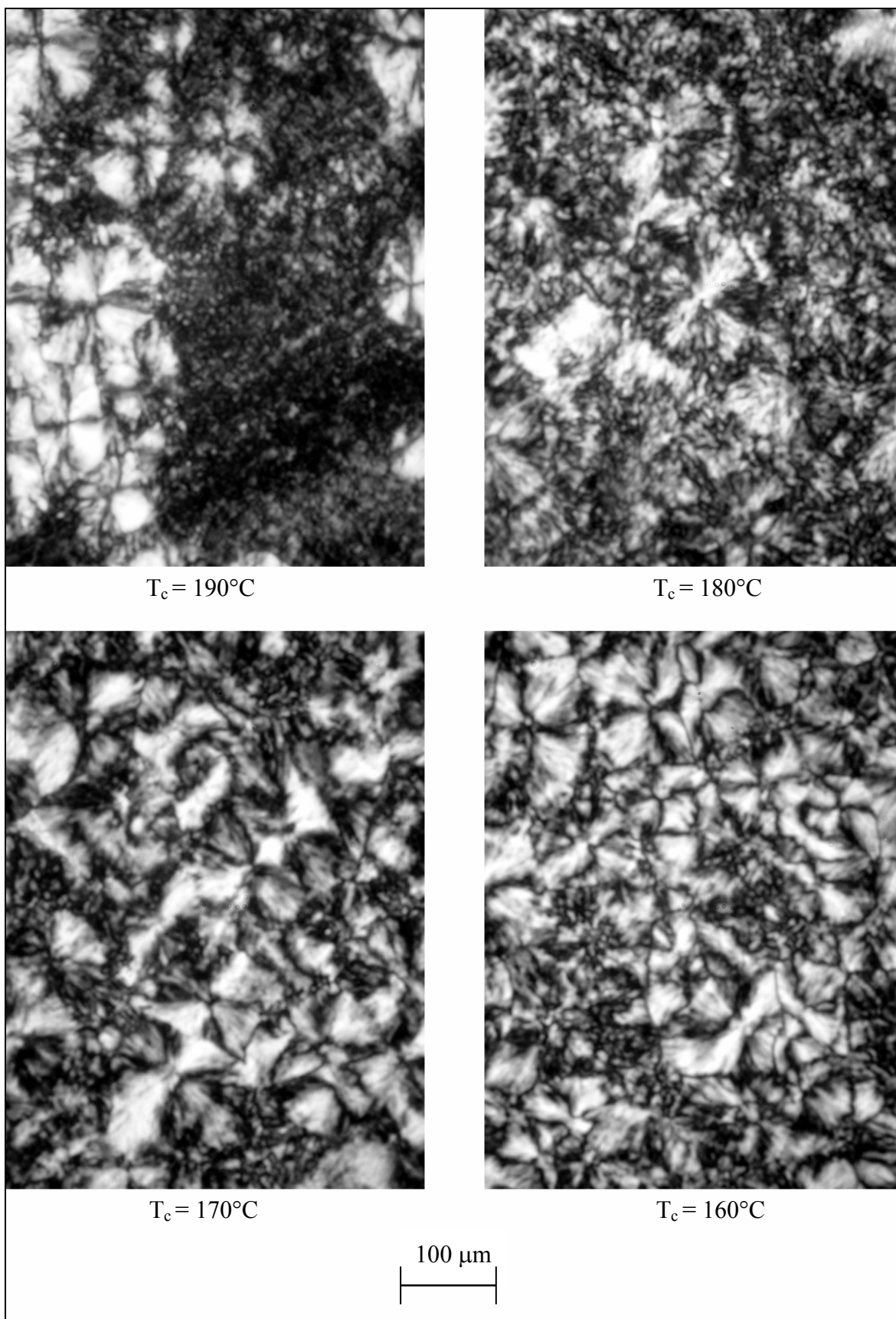
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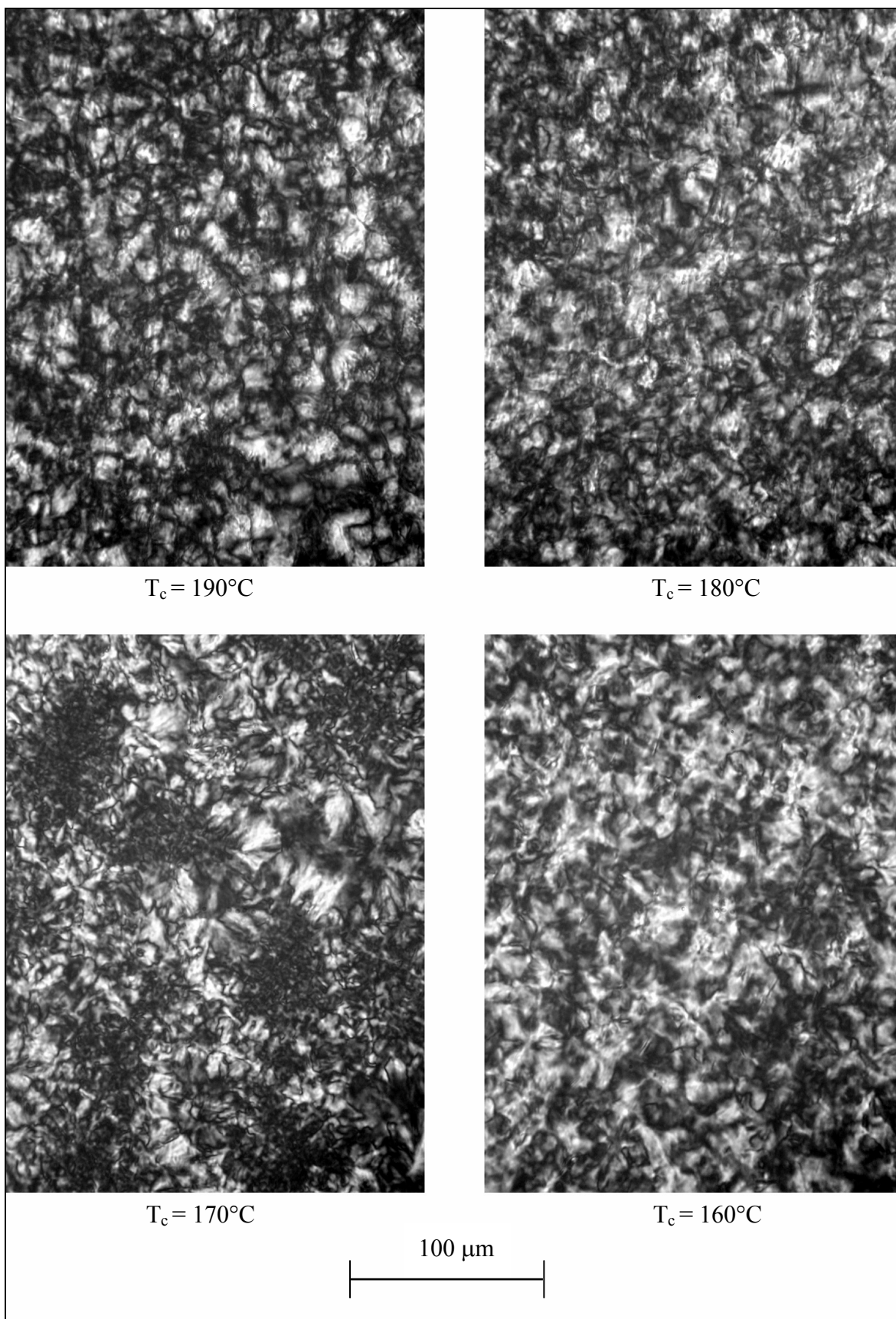
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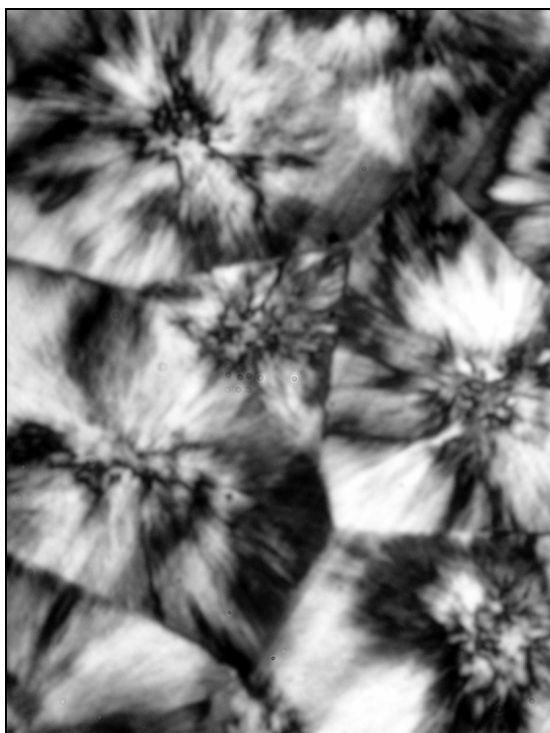
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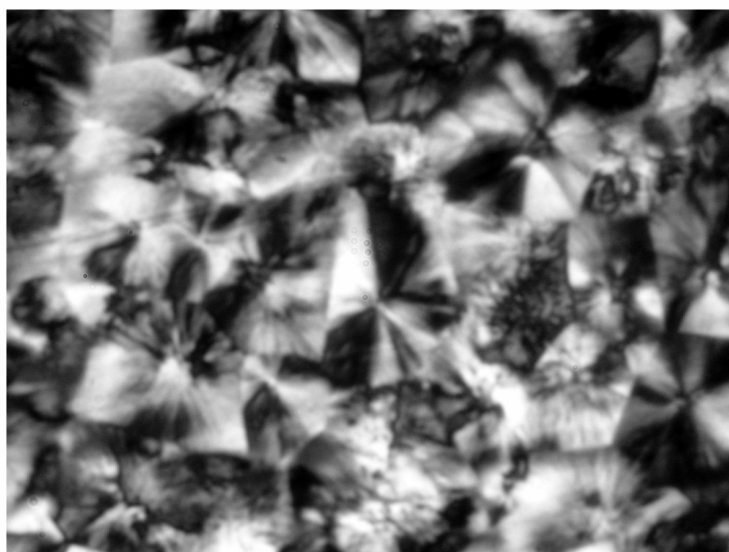
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2 °C/min



5 °C/min

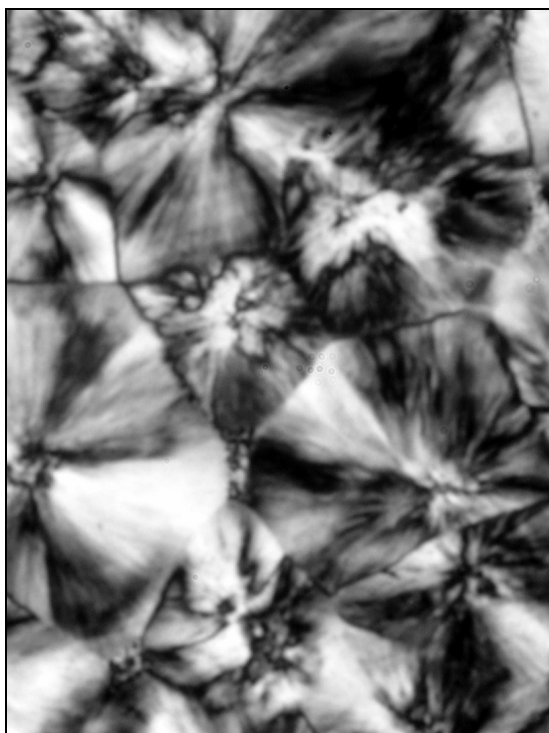


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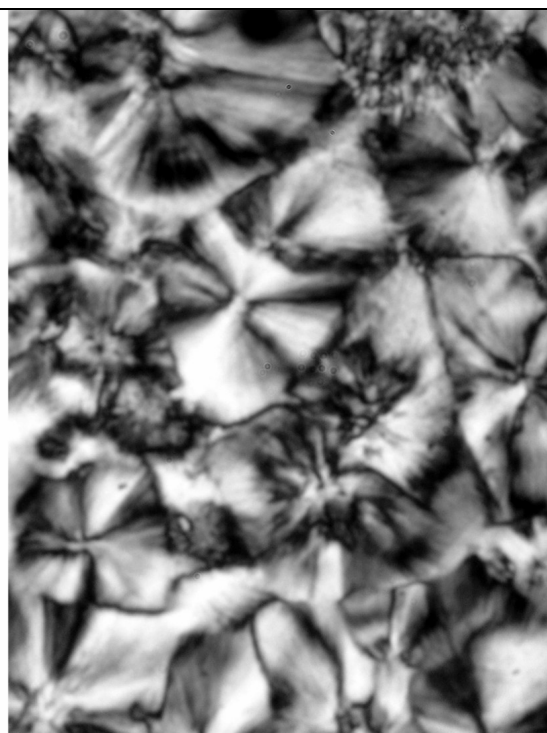
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 A horizontal scale bar with vertical end caps, representing a length of 100 micrometers.

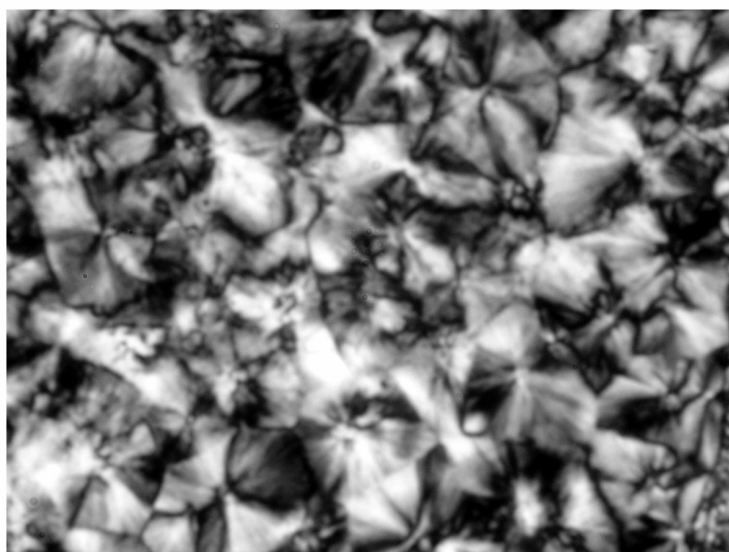
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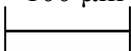


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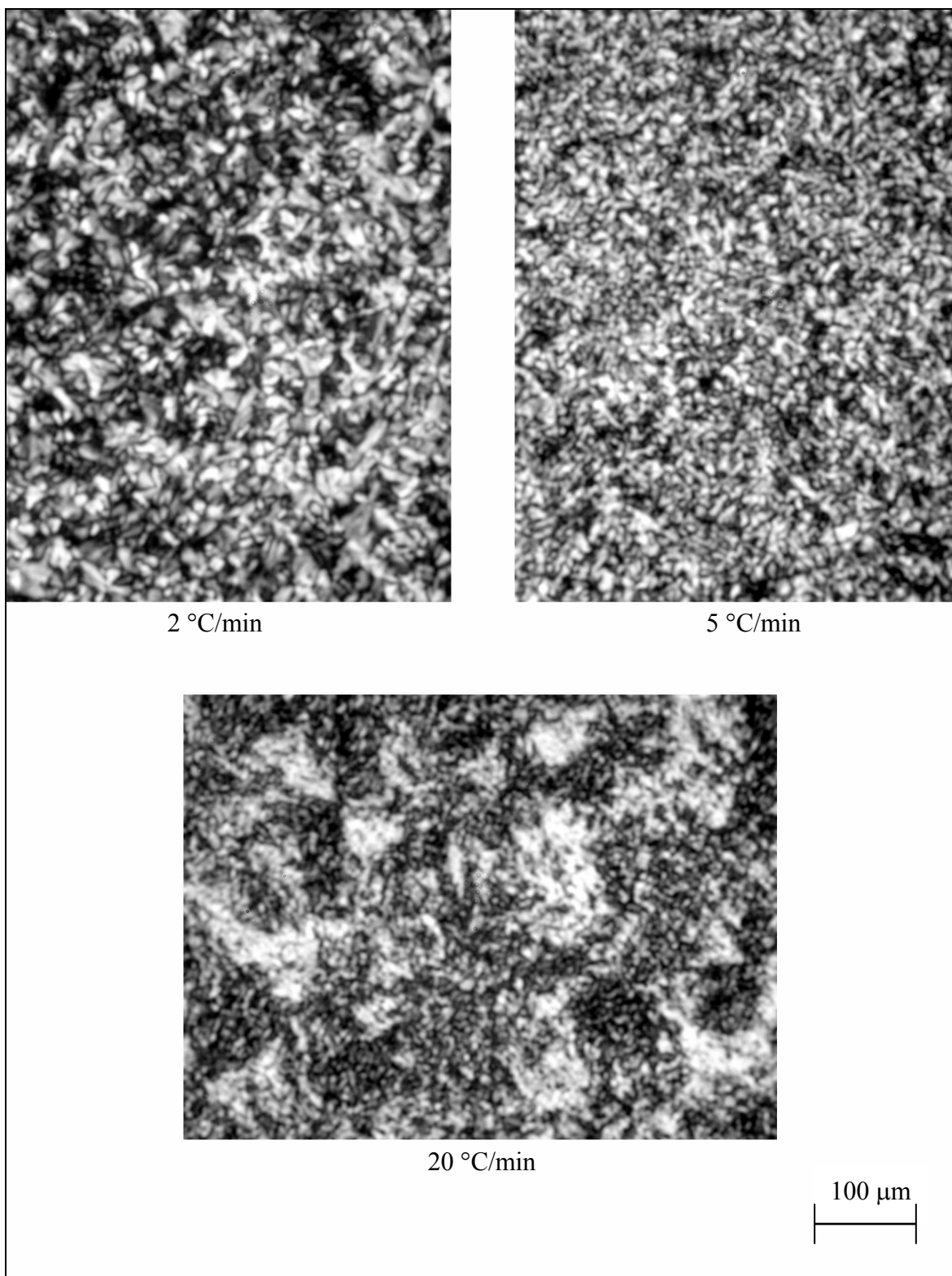


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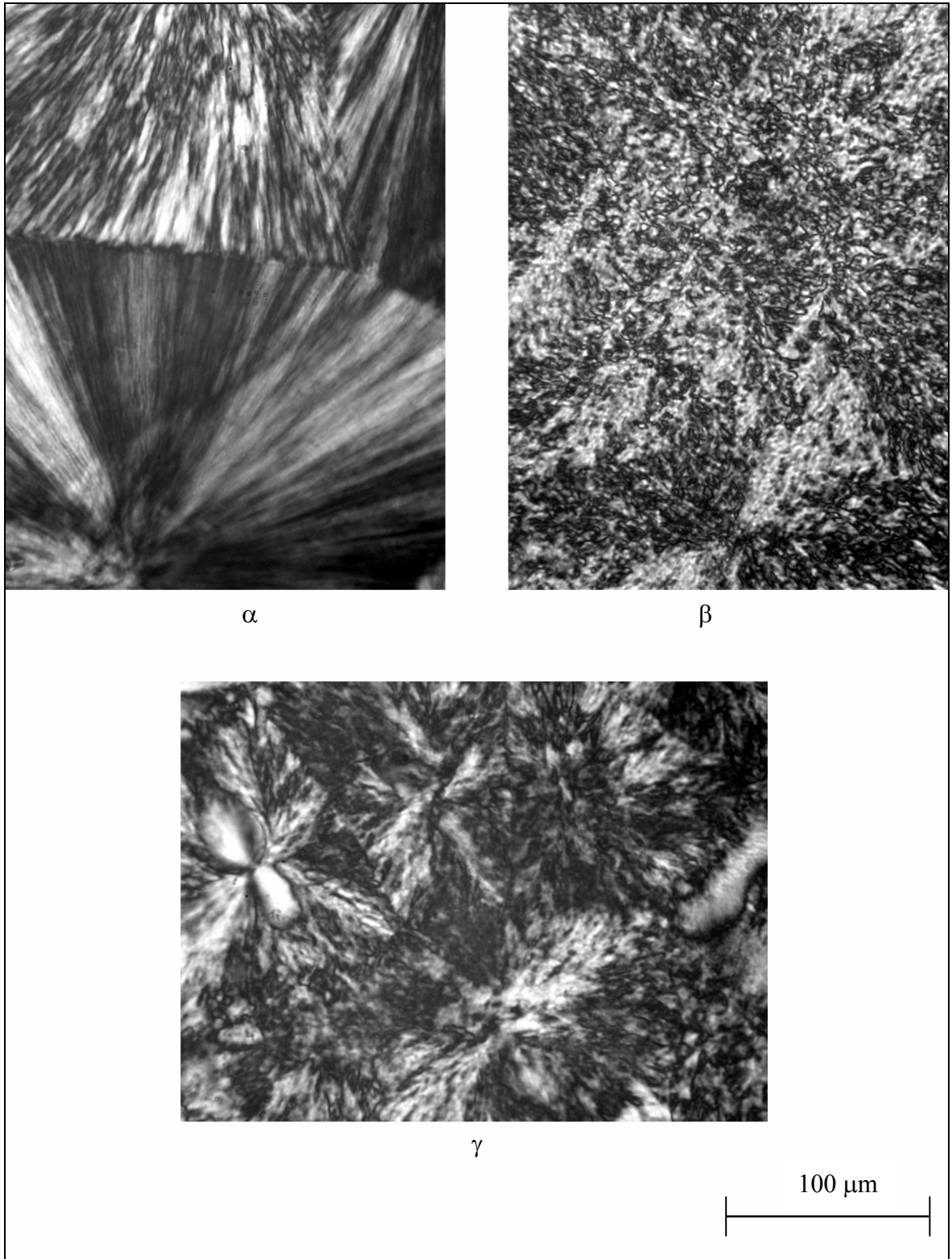
100 μm


 A horizontal scale bar with vertical end caps, indicating a length of 100 micrometers.

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**A 2: TAILORING OF MULTICOMPONENT CRYSTALLINE
SYSTEMS IN ISOTACTIC POLYPROPYLENE**

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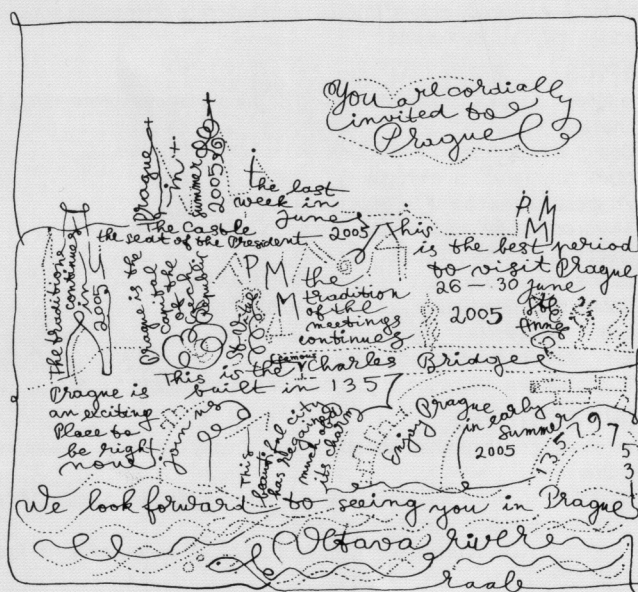
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TAILORING OF MULTICOMPONENT CRYSTALLINE SYSTEMS IN ISOTACTIC POLYPROPYLENE

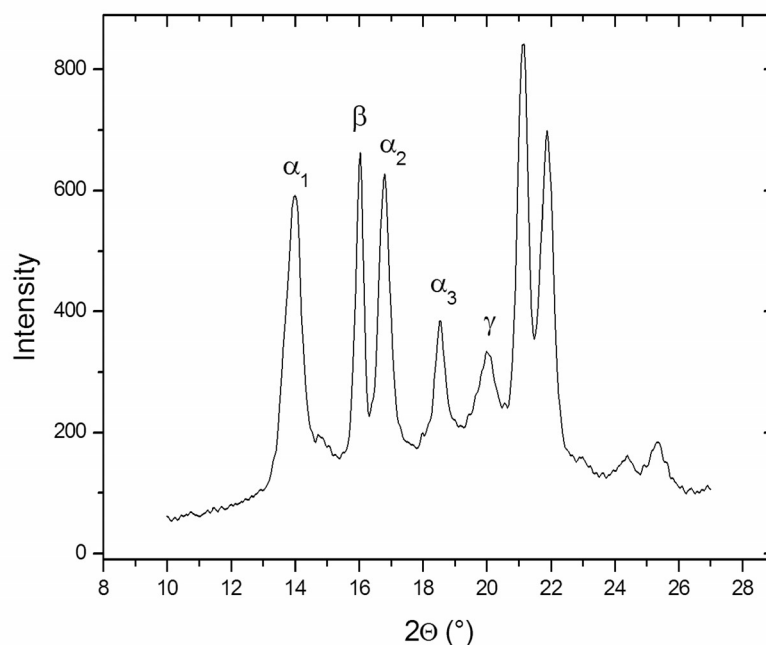
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A novel method for the preparation of unique three-phase crystalline systems in isotactic polypropylene has been proved. It is based on a synergy application of a specific β -nucleating agent and high pressure during crystallization. The γ phase formation is supported by elevated pressure and high temperature during iPP crystallization; in this case the growth of both β - and α - phase is significantly suppressed. Nevertheless, in the course of crystallization at lower pressure and/or lower temperatures, strong β -nucleation efficiency of NU100 favored the formation of β -phase. The formation of α phase was supported by the crystallization at low pressures and high temperatures.



The WAXS data indicating three-phase ($\alpha/\beta/\gamma$) crystalline system in isotactic polypropylene. The mutual phase proportions can be accurately controlled by present crystallization method.