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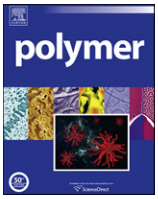

Mesophase formation in poly(propylene-*ran*-1-butene) by rapid cooling

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ABSTRACT

The effect of random insertion of low amount of 1-butene of less than about 11 mol% into the isotactic polypropylene chain on structure formation at non-isothermal crystallization at different rate of cooling was investigated by X-ray scattering, density measurements, and atomic force and polarizing optical microscopy. Emphasis is put on the evaluation of the condition of crystallization for replacement of lamellar crystals by mesomorphic nodules on increasing the cooling rate/supercooling. In the polypropylene homopolymer, mesophase formation occurs on cooling at rates larger about 150–200 K s^{-1}, while in case of poly(propylene-*ran*-1-butene) mesophase formation is observed on cooling at a lower rate of about 100 K s^{-1}. It is suggested that the lowering of the critical rate of cooling for mesophase formation in poly(propylene-*ran*-1-butene) is due to a reduction of the maximum rate of formation of monoclinic/orthorhombic crystals at low supercooling, compared to the homopolymer. The data of the present study allowed the establishment of a non-equilibrium phase diagram which shows ranges of existence of phases as a function of the cooling rate on solidification the quiescent liquid and the concentration on 1-butene co-units.

1. Introduction

Isotactic polypropylene (iPP) is a semi-crystalline polymer in which the crystalline phase can adopt different structure [1–3] and morphology as a function of the condition of crystallization [4–7]. Crystallization of the quiescent melt at low supercooling typically leads to the formation of monoclinic α-crystals which are of lamellar shape and organized in a spherulitic superstructure [4,5]. Fast cooling/high supercooling of the melt suppresses the formation of monoclinic lamellae, and leads either to formation of a mesophase [6–8], or even complete suppression of any ordering process and transformation of the entire liquid phase into a glass at the glass transition temperature [8–10].

The exact conditions for observation of fully amorphous, partially mesomorphic, or partially crystalline iPP were quantified (a) by solidification iPP at different rate of cooling using a special technique which allowed simultaneous registration of the temperature–time profile during preparation [11,12], and (b) by application of fast scanning chip calorimetry (FSC) [10,13,14]. It was found that crystallization of iPP is completely suppressed on cooling the equilibrium liquid at a rate of 10^3 K s^{-1} or faster to a temperature lower than the glass transition temperature of about 240–250 K. Cooling at a rate between about 10^2–10^3 K s^{-1} led to formation of mesomorphic non-lamellar domains/nodules at a temperature of about 300 K. The fraction of mesomorphic domains in such preparations is of the order of 30–40%, that is, the nodules are embedded in an amorphous matrix. Likely related to their instantaneous formation there is not developing any amorphous–mesomorphic superstructure, as is concluded from absence of spherulites [15,16]. Despite the mesophase is a non-equilibrium phase, it is metastable at ambient temperature and transforms into crystals or supercooled liquid only on increasing the temperature above its meta-stability limit [17,18], which recently has been quantified for the iPP homopolymer by fast scanning chip calorimetry [19]. Finally, cooling of the melt at a rate lower than about 10^2 K s^{-1} allows formation of monoclinic α-crystals at relatively low supercooling.

The present study concerns the evaluation of the effect of insertion of low amount of 1-butene co-units into the iPP macromolecule on structure formation at non-isothermal condition. There exist numerous studies about the crystallization of poly(propylene-*ran*-1-butene) (iPP-But), which, however, focused on structure formation at rather low supercooling [20–24]. Major findings of these analyses include the observation of a lowering of the crystallinity and temperatures of crystallization and melting, reduction of the maximum rate of crystallization, partial replacement of monoclinic α-crystals by orthorhombic γ-crystals, and disturbance of spherulite formation on addition of 1-butene into

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the iPP chain. From point-of-view of application of materials, these effects often are wanted since the addition of 1-alkenes into the iPP chain allows then rather easy control of thermal, mechanical or optical properties. In contrast, structure formation of poly(propylene-*ran*-1-butene) at large supercooling, as is achieved by fast cooling of the melt, similar as is evident in polymer processing, is not adequately studied yet, and is therefore objective of this work. There exist a few reports which showed that quenching the quiescent melt of poly(propylene-*ran*-1-butene), and subsequent aging at ambient temperature leads to similar formation of a mesophase as in the iPP homopolymer [25,26]. Quantitative information about the exact condition for mesophase formation, that is, cooling rate for inhibition of crystal formation is not available yet. We assume that mesophase formation in poly(propylene-*ran*-1-butene) samples can be achieved on cooling at lower rate than in case of the iPP homopolymer, with the assumption based on the experimental observations of (a) a reduced maximum rate of formation of crystals at relatively low supercooling [24], and (b) a lowered rate of cooling required for complete suppression of any ordering process in presence of chain defects [27]. The importance of the evaluation of the condition of mesophase formation from engineering science point-of-view has been demonstrated recently for the case of the iPP homopolymer. The mesophase can be considered as a precursor for generation of a specific semi-crystalline structure with a combination of optical and mechanical properties which is qualitatively different from that of conventionally crystallized material [28].

Summarizing the scope of the present study, we attempt to evaluate the relationship between cooling rate on melt solidification and structure of poly(propylene-*ran*-1-butene) of different 1-butene concentration. We employed wide-angle X-ray scattering to access the crystal structure, atomic force microscopy to obtain information about the morphology of crystals/mesomorphic domains, and polarizing optical microscopy for analysis of the superstructure. In addition, we monitored the macroscopic density of samples cooled at different rate, since it has been shown on example of isotactic polypropylene, polyamide 6, or poly(ethylene terephthalate) [11,29] that the density is an effective measure to indicate qualitative changes of the phase structure. With the present study we continue furthermore our efforts in understanding non-equilibrium mesophase formation in crystallizable polymers. Former research on low-density polyethylene, and in particular on random copolymers of ethylene and 1-octene, led to the conclusion that branches favor formation of pseudo-hexagonal mesomorphic domains [30–33]. It was found that at identical condition of crystallization/cooling rate, orthorhombic crystals were replaced by mesophase on increasing branch concentration, likely by trapping chain defects into the ordered phase. In addition, it was shown that the ratio between the fractions of crystals and of mesophase, for random ethylene-1-octene copolymers of given concentration on 1-octene, was decreasing with increasing rate of cooling. Similar investigations on iPP based random copolymers were not performed yet.

2. Experimental

2.1. Materials and preparation

Isotactic poly(propylene-*ran*-1-butene) samples with a concentration of 6.0 and 10.9 mol% 1-butene [34] (iPP-But.6 and iPP-But.11) and a mass-average molar mass and polydispersity of 225.000 g mol^{-1} and 3.1 [35], respectively, were purchased from Sigma Aldrich. The material was obtained as fine-grained powder, and processed into films with a thickness of 100 μm by compression molding, using a Collin press. Final preparation of specimens of different history of melt-crystallization, that is, cooling rate, was done as described in detail elsewhere [11,12,29]. In short, films of thickness of 100 μm and area of about 10 × 10 mm^2 were placed between a microscope-glass cover slip on one side, to obtain a smooth surface for later AFM investigation, and aluminum foil on the other side. A thermocouple was located between the polymer film and the aluminum foil for recording the temperature–time profile during preparation at high sampling rate. The sandwich was then covered by metal plates of high thermal conductivity made of a CuBe alloy. Samples were heated to 463 K, held isothermally at this temperature for a period of 5 min, and subsequently cooled at different rate to a final temperature of 288 K by spraying with cold water. The cooling history was varied via the flux of water to spray the sandwich. Since cooling is non-linear, we defined the slope of the temperature–time curve at a temperature of 343 K as cooling rate for comparison and benchmarking [29].

2.2. Instrumentation

2.2.1. Atomic force microscopy (AFM)

The morphology of crystals and mesomorphic domains of iPP-But copolymers was analyzed by AFM, using a Quesant USPM microscope with a 5 × 5 μm^2 scanner. Phase-mode images were collected at a scan rate of 4 Hz at ambient temperature with supersharp silicon tips SSS-NCL from NanoWorld. The front curvature of the tip is less than 5 nm, and the force constant and resonant frequency are 31–41 N m^{-1} and 170–210 kHz, respectively [36].

2.2.2. Polarizing optical microscopy (POM)

Presence or absence of a spherulitic superstructure was analyzed by POM, using a DMRX microscope from Leica. Images were directly obtained from the films of 100 μm thickness, that is, without further preparation.

2.2.3. Density measurement

The density of samples was measured at ambient temperature with a density gradient column from Ray-Ran, using water–ethanol mixtures of different density for preparation. The minimum and maximum density of the column, controlling the resolution, was approximately 0.886 and 0.905 g cm^{-3}, respectively. With an effective length of the column of 60 cm, and an approximate smallest increment for reading the position of the samples of 2 mm, a resolution better than 10^{-4} g cm^{-3} [= (0.905–0.886)/300] is achieved. Data presented are averages of at least three measurements.

2.2.4. Wide-angle X-ray diffraction (WAXS)

WAXS data were collected to gain information about the polymorph present in the samples of different cooling history. Intensity data were collected as function of the scattering angle on an URD 63 diffractometer from Seifert-FPM, operating in symmetric transmission mode. We used Ni-filtered Cu Kα radiation of wavelength of 0.15418 nm, and a scintillation counter for registration.

3. Results and initial discussion

Fig. 1 shows with the left, center, and right columns selected AFM phase-mode images of a larger set of preparations of iPP-But.0, iPP-But.6 and iPP-But.11, respectively, representing an area of 500 × 500 nm^2. The samples were solidified at different cooling rate between 10^{-1} K s^{-1} (top row) and 10^3 K s^{-1} (bottom row), as is indicated in the left column. Subsequently, the samples were aged at ambient temperature. The images obtained on the iPP homopolymer (left column) partially are reproductions from an earlier study [12], and were included in Fig. 1 for the sake of easy comparison of

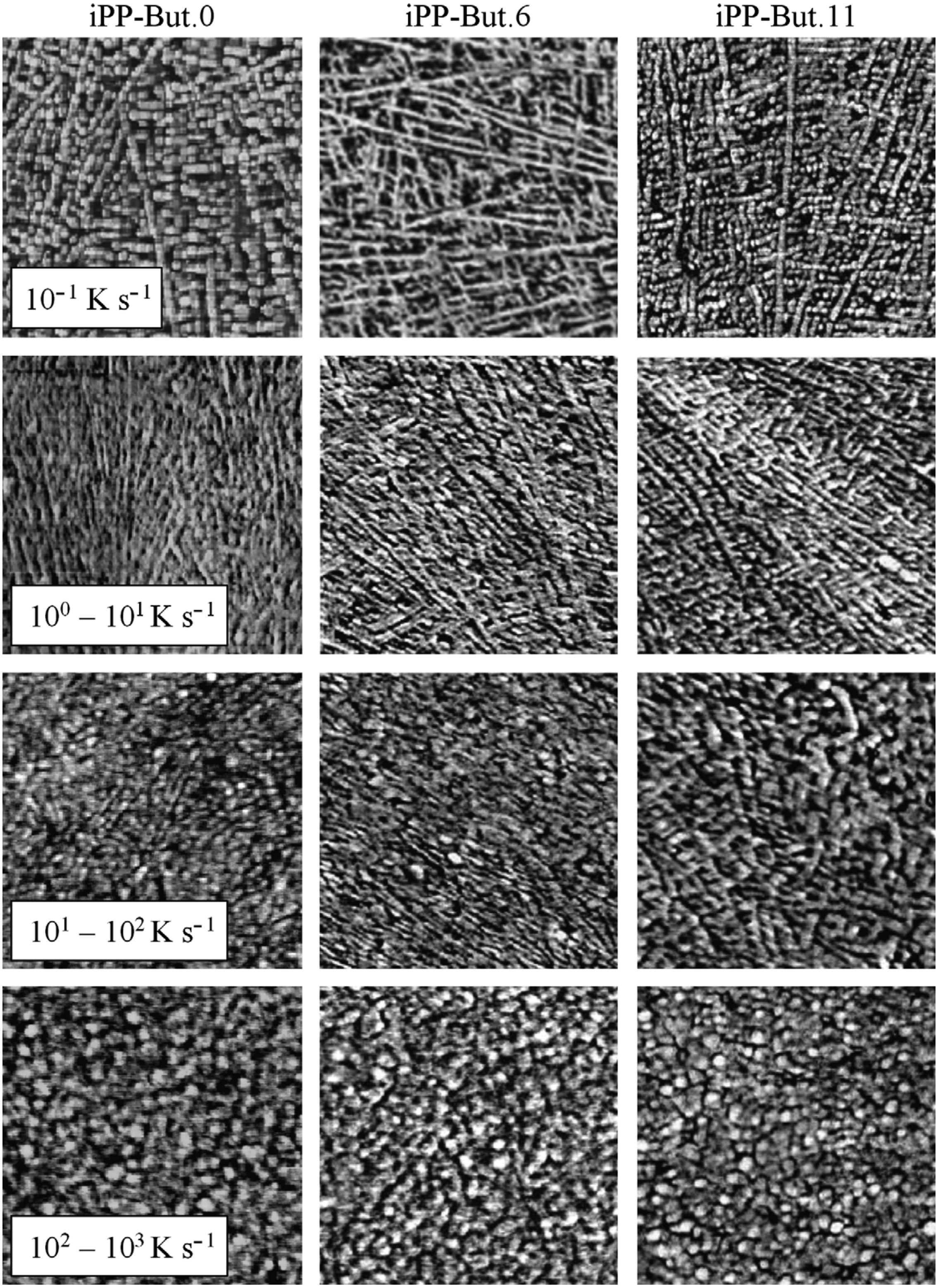

Fig. 1. AFM phase-mode images of the iPP homopolymer (iPP-But.0, left column), and poly(propylene-*ran*-1-butene) with 6 (iPP-But.6, center column) and 10.9 mol% 1-butene (iPP-But.11, right column). Samples were solidified at the indicated rate of cooling, and subsequently aged at ambient temperature. The images size corresponds 500 × 500 nm^2. Images of the left column, partially, are reproductions of an earlier study [12], and were included in this work for easy comparison with images obtained on copolymers.

the structure of the homopolymer and the copolymers. The intention of collection of AFM patterns at the specific spatial resolution was the evaluation of the structure at the nanometer scale, which provides information about the habit of crystals/domains. The images of Fig. 1 reveal formation of lamellae on cooling at rates lower than 10^1 K s^{-1}, coexistence of lamellae and nodules on cooling between about 10^1–10^2 K s^{-1}, and exclusive formation of nodules on cooling at rates higher than 10^2 K s^{-1}. This classification is true for both the homopolymer and iPP-But copolymers with a maximum concentration of 1-butene of close to 11 mol%. The size of lamellae in the slowly cooled preparation seems to decrease with increasing concentration of 1-butene, and confirms an earlier quantitative investigation of the effect of 1-butene co-units on the thickness of lamellae formed on linear cooling at 10 K min^{-1} [25]. More important in the context of the present study of analysis of structure formation at rapid cooling is the replacement of lamellar crystals by isometric nodules in the iPP-But copolymers on increasing the rate of cooling, similar as in the homopolymer. The size of nodules is about 10–20 nm, apparently being independent on the concentration of 1-butene co-units.

Fig. 2 shows the structure of samples of different history of cooling and concentration of 1-butene co-units at the micrometer scale, as was assessed by polarizing optical microscopy (POM). Samples which were cooled at rates between 10^{-1} and 10^{1} K s^{-1} (top two rows) show a spherulitic superstructure, regardless the concentration on 1-butene. The size of spherulites decreases with increasing concentration on 1-butene and with increasing rate of cooling. Further increase of the cooling rate to about 20 K s^{-1} (third row, 10^{1}–10^{2} K s^{-1}) results in formation of qualitatively different superstructures in samples of different 1-butene concentration. While in case of the iPP homopolymer spherulite formation is detected, though not space filling, in case of the copolymers spherulites are either extremely small or almost completely absent. Finally, if samples were solidified at a rate faster than 10^{2} K s^{-1} (bottom row), then spherulites are not formed in all of the samples investigated.

The experimental observations of Fig. 2 agree with former investigations regarding (a) the relation between the microstructure and history of crystallization performed on a different specific iPP homopolymer [11], and (b) the effect of addition of 1-butene on

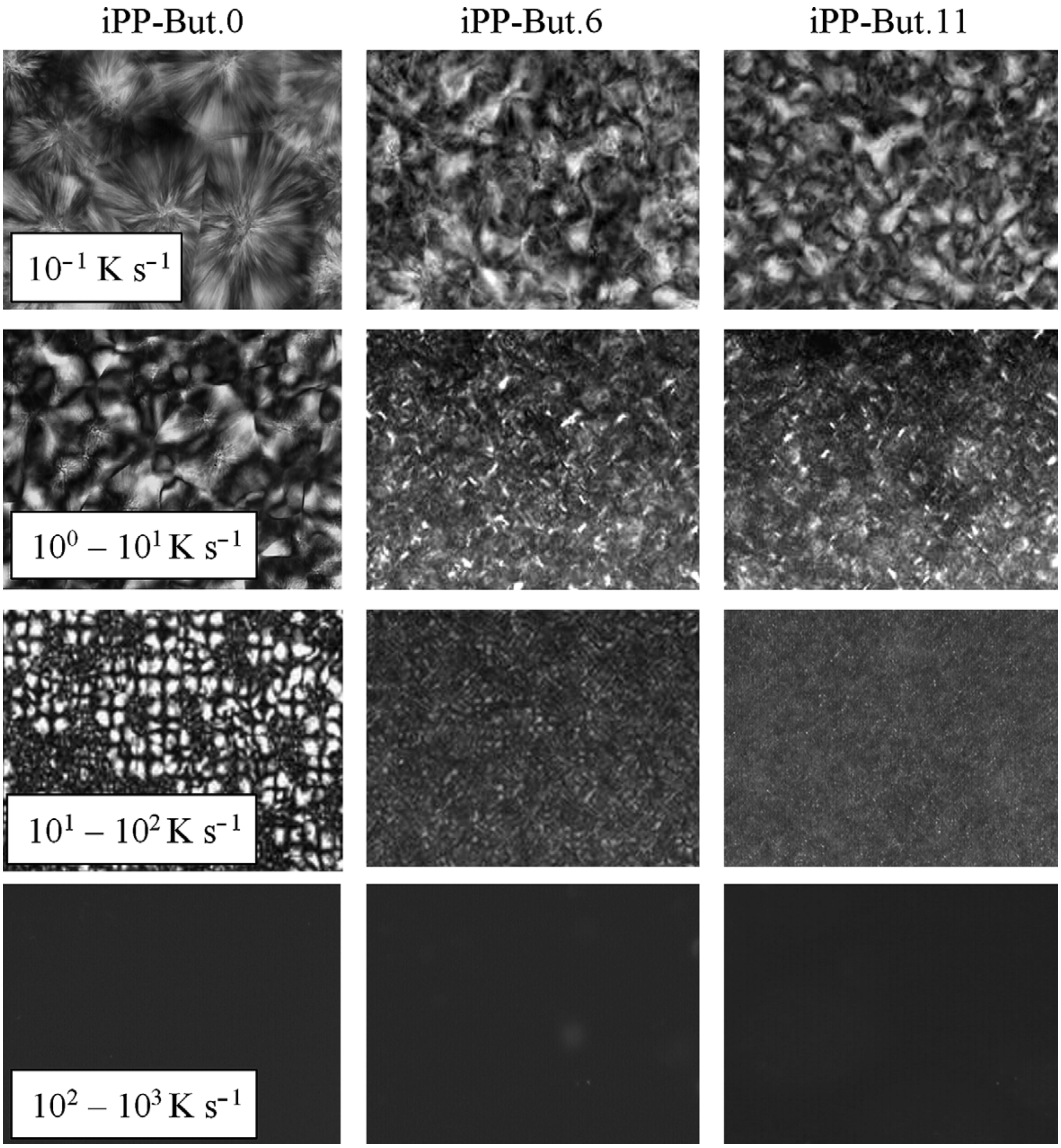

Fig. 2. Polarizing optical micrographs of the iPP homopolymer (iPP-But.0, left column), and poly(propylene-*ran*-1-butene) with 6 (iPP-But.6, center column) and 10.9 mol% 1-butene (iPP-But.11, right column). Samples were solidified at the indicated rate of cooling, and subsequently aged at ambient temperature. The image width corresponds 130 µm. Images of the left column partially are reproductions from an earlier study [12], and were included in this work for easy comparison with micrographs obtained on copolymers.

spherulite formation at slow and fast cooling [16]. As such, the advance of the POM part of the present study is the quantification of the relation between the exact cooling rate on solidification and structure formation in the iPP-But copolymers. The comparison of the optical micrographs with the AFM images leads to the conclusion that spherulite formation is inevitable connected with occurrence of lamellae while in case of presence of isometric particle-like nodules spherulite formation is not observed. Absence of higher-order organization in the latter case points to simultaneous non-correlated appearance of the majority of nodules, which provides no option for their spatial alignment as a prerequisite for observation of a superstructure and a macroscopic birefringence pattern.

Fig. 3 shows WAXS data, intensity as a function of the scattering angle, of samples of iPP-But.0 (left), iPP-But.6 (center), and iPP-But.11 (right), solidified at the indicated cooling rate, and subsequently aged at ambient temperature. WAXS data were collected to obtain information about the internal structure of the lamellae or nodules, as were observed by AFM. Slow cooling at rates lower than about 50 K s^{-1} results in formation of monoclinic α-crystals in both the iPP homopolymer and the iPP copolymers, as can be concluded from the presence of the characteristic diffraction peaks [1,2]. In case of the copolymers, additional formation of the orthorhombic γ-polymorph was detected by presence of an additional diffraction peak in samples which were cooled at 0.1 K s^{-1}. The observation of γ-crystals is in agreement with several studies reported in the literature. The γ-structure is suggested to accommodate larger amount of co-units/chain defects than the monoclinic α-phase and develops preferred at rather low supercooling [21,22,37]. Obviously, the γ-phase does not form if the cooling rate is equal or higher than 10 K s^{-1}. Qualitative inspection of the X-ray scans, obtained on samples crystallized at similar, rather low cooling rate, reveals a slight decrease of the degree of crystallinity with increasing concentration of co-units, as is expected from former research [22,25]. Furthermore, there is observed a dilatation of the monoclinic lattice in the copolymers, likely due to inclusion of 1-butene units [21,25].

Cooling at rates faster than about 50 K s^{-1} leads to suppression of formation of monoclinic crystals, as is concluded from the disappearance of the corresponding diffraction peaks in the X-ray patterns. Instead, development of mesophase is detected by observation of two characteristic halos [38,39]. Comparison of the X-ray data of the various polymers of different concentration of co-units, solidified by cooling at a rate of about 40–50 K s^{-1}, suggests coexistence of mesophase and monoclinic structure in the iPP homopolymer while in the copolymers scattering from the monoclinic phase seems absent. A further increase of the cooling rate up to 10^3 K s^{-1} is not connected with a qualitative change of the patterns. Interestingly, we detected a shift of the halo at about 14.8° scattering angle, which is related to the average inter-chain distance within the pseudo-hexagonal mesophase [38,39], toward a lower angle with increasing concentration of co-units. In other words, 1-butene co-units may enter the mesophase, and cause an expansion in cross-chain direction and a lowering of the bulk density. The detailed characterization of the structure and thermodynamic properties/melting temperature of the mesophase is part of a companion study, and is presented separately. According to the WAXS results of Fig. 3, we conclude that lamellar crystals of slowly cooled preparations, as obtained by AFM, exhibit a monoclinic symmetry, while nodular domains are of mesomorphic structure.

Fig. 4 shows the macroscopic density of the iPP homopolymer (iPP-But.0, star symbols), and of the copolymers iPP-But.6 (open squares) and iPP-But.11 (filled squares) as a function of the cooling rate on solidification the quiescent liquid. The density of amorphous iPP is 0.8665 g cm^{-3}, and the densities of the monoclinic crystalline phase and pseudo-hexagonal mesophase are 0.9405 and 0.920 g cm^{-3}, respectively [40]. The experimentally observed density of the specimens of the present study is about 0.9 g cm^{-3} after slow cooling at rates lower than about 10^1 K s^{-1}, and about 0.89 g cm^{-3} after rapid cooling at rates faster than about 10^2 K s^{-1}. The density data of all samples show a sigmoidal dependence on the cooling rate, that is, there is observed a step-like decrease of the density on increasing the cooling rate in a rather narrow range at about 10^1 K s^{-1}. It has been shown in previous research that the step-like decrease of the density from a high-level plateau at low cooling rate to a low-level plateau at high cooling rate is due to the replacement of monoclinic crystals by mesomorphic structure [11,12,29,40], both coexisting with amorphous phase. The X-ray data of Fig. 3 unambiguously confirm this interpretation of the density data.

In extension to previous work, the focus of the present investigation is the evaluation of the effect of the addition of 1-butene co-units on the crystallization behavior. First of all, presence of 1-butene co-units results in a decrease of the fraction of monoclinic/orthorhombic crystals after solidification at low cooling rate. This is indicated in Fig. 4 with the downward directed arrow. Density data of 0.902 g cm^{-3}, observed for iPP-But.0, and 0.898 g cm^{-3}, observed for iPP-But.11, both after slow cooling, correspond to fractions of monoclinic crystals within the semi-crystalline structure of about 48 and 43%, respectively. A similar trend of a decrease of the crystallinity with increasing 1-butene content has been observed by calorimetry [25], after samples were crystallized during linear cooling at 10 K min^{-1}. Note that we are aware of a minor underestimation of the fraction of monoclinic crystals in the copolymers since there is observed a slight decrease of the crystal density due to the incorporation of defects. In fact, it may be possible that

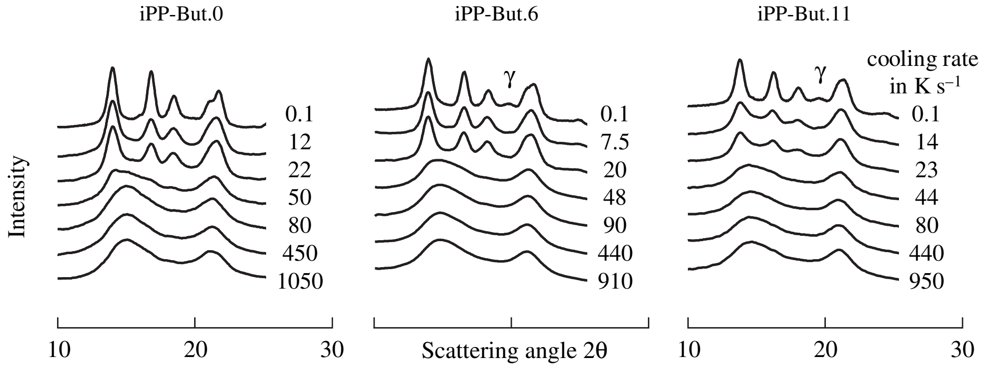

Fig. 3. WAXS data of the iPP homopolymer (iPP-But.0, left plot), and poly(propylene-*ran*-1-butene) with 6 (iPP-But.6, center plot) and 10.9 mol% 1-butene (iPP-But.11, right plot). Samples were solidified at the indicated rate of cooling, and subsequently aged at ambient temperature.

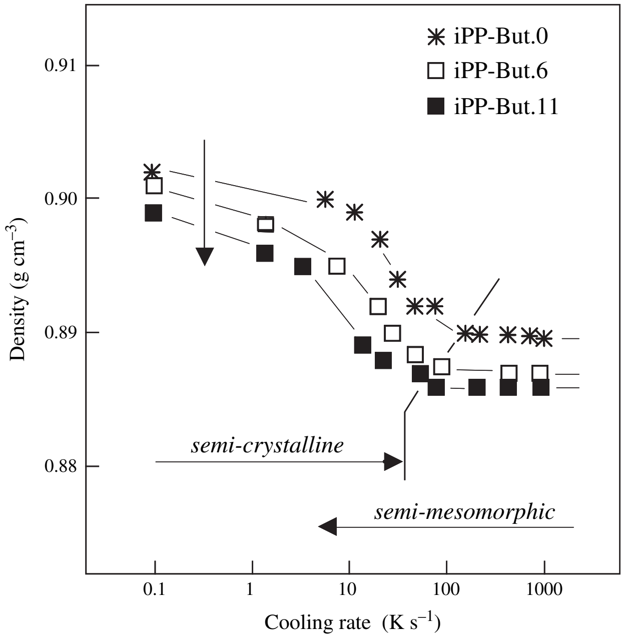

Fig. 4. Density of the iPP homopolymer (iPP-But.0, star symbols), and poly(propylene-*ran*-1-butene) with 6 (iPP-But.6, open squares) and 10.9 mol% 1-butene (iPP-But.11, filled squares) as a function of the cooling rate on solidification the quiescent liquid.

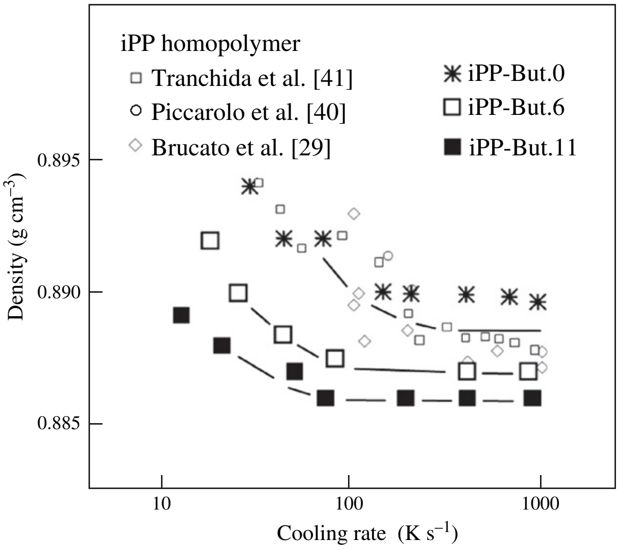

Fig. 5. Enlargement of Fig. 4. Density of the iPP homopolymer (iPP-But.0, star symbols), and poly(propylene-*ran*-1-butene) with 6 (iPP-But.6, open squares) and 10.9 mol% 1-butene (iPP-But.11, filled squares) as a function of the cooling rate on solidification the quiescent liquid. The graph contains additional data available in the literature [29,40,41], obtained on different grades of iPP.

crystalline fractions in the homopolymer and the copolymers are close-to-identical as also has been suggested in the literature [21]. Furthermore, the density data decrease slightly with increasing rate of cooling within the high-level plateau, which likely is a purely kinetic effect. In this case, there is no space for speculation whether the decrease of the density is due to a decrease of fraction of crystals or decrease of the crystal density, since X-ray data do not show a variation of the position of diffraction peaks in samples of different cooling history.

The density values obtained in rapidly cooled samples show a similar decrease with increasing concentration of co-units. We observed a density of 0.889 g cm^{-3} in case of the homopolymer, and values of 0.886 and 0.885 g cm^{-3} in case of the copolymers iPP-But.6 and iPP-But.11, respectively. The data are independent on the exact cooling rate, which is due to mesophase formation at identical, namely ambient temperature during isothermal ageing. The density data of 0.889, 0.886, and 0.885 g cm^{-3} of the different polymers of the present study after fast cooling and aging at ambient temperature can be recalculated into fractions of mesomorphic domains of 42, 36, and 35%, respectively. These values, however, only would be true if the density of the mesophase is not a function of the concentration of 1-butene co-units in the chain. Since we have observed an increase of the inter-chain distance in the mesophase of the copolymers by X-ray diffraction, an ultimate interpretation is not yet possible, and the true fraction of mesophase in the copolymers may be higher than the values provided above.

Finally, the density data of Fig. 4 provide information about the effect of 1-butene co-units on the minimum rate of cooling which is required for complete suppression of formation of monoclinic crystals. The formation of monoclinic crystals is indicated by observation of a macroscopic density which is higher than the density in the low-density plateau region of rapidly cooled specimens. The onset of the increase of the density on decreasing cooling rate is indicated in Fig. 4, and occurs in case of the iPP homopolymer at higher rate than in case of the copolymers. Note that the density data in Fig. 4 were plotted as a function of the logarithm of the cooling rate, apparently pretending an only minor or negligible effect. Formation of monoclinic crystals occurs in case of the iPP homopolymer only if cooling is performed at a rate of 160 K s^{-1}, [10] or lower, while in case of the copolymers with 6 and 10.9 mol% 1-butene formation of monoclinic crystals requires cooling at rates lower than 90 or 80 K s^{-1}, respectively [27]. Correspondingly, if the cooling rate is higher than these values, the samples do not contain monoclinic crystals, rather than are composed of amorphous structure and mesophase.

Further support of the observation of different condition of cooling for suppression of monoclinic crystal formation in random copolymers of iPP with 1-butene, in comparison to the iPP homopolymer, is provided with Fig. 5. It is an enlargement of Fig. 4 and is intended to show the first increase of density above the level of the low-density plateau on lowering the cooling rate at about 100 K s^{-1}. The graph contains with the small symbols additional density data obtained on iPP of different grade/source, available in the literature [29,40,41]. The literature data were included in order to proof that the observed different onset of crystal formation on lowering the cooling rate of the polymers of this study, discussed in Fig. 4, is not only true on using the specific iPP of the present study for analysis, rather is a general information. Note that reports in the literature suggest an effect of the molecular characteristics such as tacticity on the crystallization/mesophase formation behavior in iPP [42], which urgently recommends employment of a larger set data to gain confidence. Regarding additional data obtained on random iPP-But copolymers, no further studies are available in the literature.

4. Final discussion and conclusions

The focus of the present study is the evaluation of the effect of random insertion of low amount of 1-butene co-units into the iPP macromolecule on structure formation at non-isothermal condition. While crystallization of random iPP-But copolymers at low supercooling, which is equivalent to non-isothermal crystallization at slow cooling, has extensively been studied in the past e.g. by the research groups of De Rosa [21], or Alamo [22–24], we put special emphasis on the analysis of crystallization at rapid cooling. It was found that rapid cooling of the iPP homopolymer leads to a replacement of monoclinic lamellae by mesomorphic nodules [3,6–8,11,12], or even complete inhibition of any ordering process, that is, also mesophase formation [8–10,13]. A stringent precondition for inhibition of mesophase formation, that is, complete transformation of the supercooled liquid into a glassy state is sufficiently fast cooling to a temperature lower than the glass transition temperature.

In a recent work, we studied the effect of addition of 1-butene co-units on the minimum rate of cooling required for complete transformation of the supercooled liquid into the glassy state, using fast scanning chip calorimetry (FSC) [27]. It was found that the addition of 1-butene reduces the critical cooling rate to obtain a fully glassy polymer, which is in accord with the general observation of a lowering of the temperature and maximum rate of crystallization in random olefin-1-alkene copolymers compared to the homopolymer, quantitatively evidenced for the particular case of iPP-But copolymers by the work of Alamo [24]. Further completion of the research about structure formation of iPP-But copolymers at rapid cooling is attempted with the present study, which in particular is intended to gain information about the conditions of cooling for replacement of monoclinic lamellar crystals by mesomorphic nodules on increasing the cooling rate. To achieve this goal, we prepared films by cooling the quiescent liquid to ambient temperature at different rates between 10^{-1} and 10^3 K s^{-1} and analyzed the structure by microscopy, WAXS, and density measurements.

The experimental observations of this study consistently proof that the change of structure from formation of monoclinic lamellae within a spherulitic superstructure to formation of mesomorphic non-lamellar domains without spherulitic organization is qualitatively not affected by random insertion of low amount of 1-butene co-units into the iPP chain. The AFM and POM images of Figs. 1 and 2 prove replacement of lamellar crystals by nearly isometric, nodular domains, and disappearance of spherulite formation, respectively, on increasing the cooling rate between 10^1 and 10^2 K s^{-1}. The WAXS data of Fig. 3, correspondingly, provide the information that lamellae exhibit monoclinic structure and that the nodules are mesomorphic. Exceptions are copolymers which were cooled at low rate and which partially contain orthorhombic crystals.

Quantitative information about the relation between the cooling rate and formation of specific polymorphs as a function of the comonomer content were gained from density measurements. The increase of the density on lowering the cooling rate in the range between 10^3 and 10^1 K s^{-1} is due to formation of monoclinic crystals, either by replacing mesomorphic domains or supercooled liquid, as is concluded from the WAXS data, and being in accord with a previous study about exact phase fractions in the iPP homopolymer, solidified at different rate of cooling [38]. The density data of Figs 4 and 5 show that complete suppression of formation of monoclinic crystals is achieved at a lower cooling rate if 1-butene co-units are present in the iPP chain. This result is supported by the POM micrographs of Fig. 2 which clearly showed strongly different extinction pattern for specimens of different 1-butene concentration, solidified at identical cooling rate of about 10^2 K s^{-1}.

The data of the present study allow to complete a non-equilibrium phase diagram, which provides qualitative information about the phase structure of iPP as a function of the concentration of 1-butene co-units, and a as function of the cooling rate used to solidify the equilibrium liquid. Such a representation of ranges of existence of the various phase structures of iPP and iPP-But copolymers is shown in Fig. 6, summarizing recent research in this field [10,27], together with results of the present study. In Fig. 6 is illustrated that cooling at a rate faster than indicated with the top line, to a temperature lower than the glass transition temperature, results in formation of a fully amorphous glass. In contrast, cooling at rates lower than indicated with the bottom line allows formation of monoclinic/orthorhombic crystals and a semi-crystalline spherulitic superstructure. Finally, formation of mesophase and a semi-mesomorphic non-spherulitic superstructure is observed if samples are cooled at a rate which is indicated in Fig. 6 by range (2). Typical examples of such structures are shown at the right with the inserted AFM and POM images, initially shown in Figs. 1 and 2. Extrapolation of the critical rate of cooling for suppression of crystallization and/or mesophase formation to distinctly higher concentration on 1-butene is not recommended. Crystallization and mesophase formation may completely be absent at high concentration on co-units, or perhaps new crystal structures may develop at a rate which is different from that of formation of monoclinic or orthorhombic crystals.

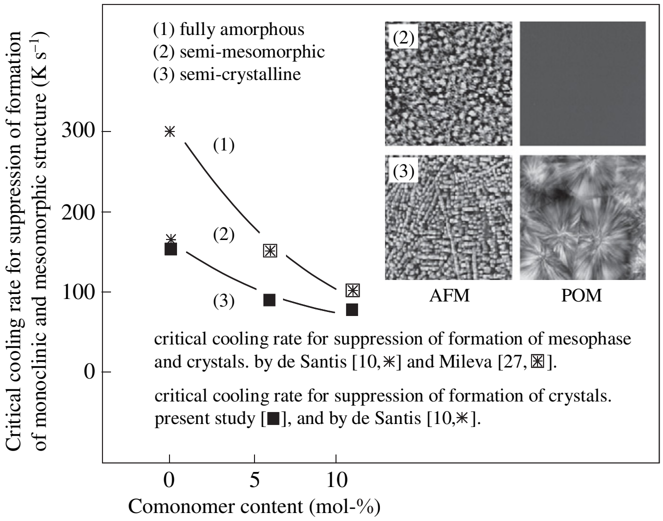

Fig. 6. Critical rate of cooling for (a) complete suppression of mesophase and crystal formation (top line) and (b) complete suppression of crystal formation (bottom line) as a function of the concentration of 1-butene co-units. The AFM and POM images serve for easy recognition of the main difference of semi-crystalline spherulitic and semi-mesomorphic non-spherulitic structures, to be obtained by cooling at the specified rates.

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