

## X-ray study of crystallization of random copolymers of propylene and 1-butene via a mesophase

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### ABSTRACT

Wide-angle X-ray scattering has been employed for evaluation of the crystal structure of cold-crystallized random copolymers of propylene with 1-butene. The crystallization procedure included the formation of a metastable mesophase at ambient temperature by quenching the quiescent melt, and the reorganization of the semimesomorphic structure into a semicrystalline structure on subsequent heating/annealing. Research was performed to gain information about incorporation/exclusion of 1-butene chain defects into the crystalline phase when formed via the intermediate step of mesophase formation. The X-ray data suggest that 1-butene co-units up to a concentration of at least 11 mol-% are incorporated into both the mesophase formed on quenching and crystals formed on subsequent heating/annealing according to their concentration in the chain. This observation is in agreement with results obtained on samples which were crystallized directly from the supercooled liquid state, indicating that incorporation of 1-butene co-units into the crystalline phase is not kinetically controlled. Furthermore, information about the  $\alpha/\gamma$  polymorphism and the kinetics of the transition from the semimesomorphic into semicrystalline structure are provided.

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### 1. Introduction

The structure and properties of isotactic polypropylene (iPP) can effectively be controlled by random insertion of 1-butene co-units into the iPP chain. Presence of even low amount of 1-butene co-units in the iPP macromolecule affects drastically the crystallization behavior and the mobility of the amorphous chain segments. The glass transition temperature, crystallization and melting temperatures, crystallization rate, and crystallinity are decreased in random copolymers of isotactic polypropylene with 1-butene (iPP-But) which ultimately can be utilized to generate new polypropylene-based materials for specific applications [1,2]. Prerequisite for development of new materials, however, is a detailed knowledge about the relationship between the chemical structure of the macromolecule/co-unit concentration, the condition of processing/crystallization, the resulting physical structure, and the properties of the copolymers. In the present work, emphasis is placed on gaining information about the relation between the condition of crystallization and the fine structure of the crystal phase in random copolymers of propylene

with up to 11 mol-% 1-butene. Quantitative information about the effect of presence of constitutional defects in the iPP chain on the structure of the crystalline phase are available for the specific cases of solution crystallization [3] and melt crystallization, that is, direct transformation of the supercooled liquid into crystals [4–12]. In contrast, at present there exist only limited data about the crystal structure if crystals were formed via the intermediate stage of a metastable mesophase, that is, via rapid cooling of the melt and subsequent cold crystallization [13,14].

Fundamental studies about the crystallization process of iPP-But random copolymers — in particular the  $\alpha/\gamma$  polymorphism — have been performed by the groups of De Rosa [7] and Alamo [8–10]. Regarding the crystal structure, it was consistently found that presence of 1-butene co-units in the iPP macromolecule at concentrations lower than about 10 mol-% leads to formation of both monoclinic  $\alpha$ - and orthorhombic  $\gamma$ -crystals, with the relative fractions being dependent on the crystallization temperature and absolute concentration on co-units. The fraction of  $\gamma$ -crystals was increasing with increasing temperature of crystallization and with increasing content on 1-butene. Melt crystallization of the iPP homopolymer at low supercooling typically leads to formation of spherulites [15,16], in which monoclinic  $\alpha$ -crystals of lamellar shape are oriented parallel and perpendicular to the spherulite radius due

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to so-called cross-hatching, that is, due to lamellar branching/homo-epitaxial growth of daughter lamellae on parent lamellae at specific crystallographic planes [17,18]. The orthorhombic  $\gamma$ -phase was first detected in iPP of low molecular weight [19], however, also forms on crystallization at elevated pressure [20–22] and — more important in the context of the present study — has frequently been observed in crystallizing propylene copolymers [4,23]. It is suggested that  $\gamma$ -crystal formation in random copolymers is due to interruptions of the regular sequences of isotactic polypropylene, that is, due to presence of co-units and presence of regio- and stereo-defects [24]. Typically, melt crystallization of random copolymers at atmospheric pressure does not lead to exclusive formation of  $\gamma$ -crystals rather than  $\gamma$ -crystals co-crystallize in conjunction with  $\alpha$ -crystals. Electron microscopy and electron diffraction studies indicated that  $\gamma$ -crystals growth epitaxially at the lateral surface of  $\alpha$ -crystals comprising the (010) lattice plane [25].

Furthermore, it was found that in both  $\alpha$ - and  $\gamma$ -crystals of as-synthesized [7], solution-crystallized [3], and melt-crystallized random iPP-But copolymers [7–12] the unit cell is expanded, with the volume increase being different in the various crystallographic directions, and being proportional to the total concentration of such chain defects. The unit cell expansion mainly was observed in direction of stacking of bilayers of chains in both  $\alpha$ - and  $\gamma$ -crystals [26,27], that is, in direction of the  $b$ -axis of the monoclinic  $\alpha$ -crystal, and the  $c$ -axis of the orthorhombic  $\gamma$ -structure. Note that the  $c$ -axis of the  $\gamma$ -structure is not parallel to the chain direction. It was concluded that 1-butene co-units are equally incorporated into  $\alpha$ - and  $\gamma$ -crystals, at least up to a total comonomer concentration of about 10 mol-% [7]. In addition, using a fuming nitric acid etching technique in combination with  $^{13}\text{C}$  NMR spectroscopy, it was found that the amount of 1-butene included in the crystalline phase is comparable with the amount present in the amorphous phase [11], that is, there is equal partitioning of 1-butene co-units in the crystalline and amorphous phases. In contrast, ethylene, 1-hexene, and 1-octene are incorporated into the  $\alpha$ - and  $\gamma$ -phases to lesser amount than 1-butene [7,8,11,28,29], that is, the concentration of co-units in the crystalline phase is lower than in the amorphous phase. As a consequence, the partial exclusion of ethylene, 1-hexene, and 1-octene co-units from crystallization leads to a decrease of the crystallization rate, compared to the iPP homopolymer and iPP-But random copolymers of similar concentration on co-units [8]. Comparison of the unit cell expansion of crystals obtained from dilute solution and from the melt indicated that the process and mechanism of crystal formation seem independent of the exact crystallization route [3], that is, one can speculate that 1-butene co-units are included into the crystals without segregation.

Melt crystallization is the transformation of supercooled liquid into crystals at a temperature between the glass transition temperature and the equilibrium melting temperature. It is typically performed on cooling the equilibrium liquid, however, includes the specific case of cold crystallization which is synonymous for 'melt crystallization on heating from below the glass transition temperature'. Crystallization on heating/cold crystallization occurs if the conditions of prior cooling of the liquid polymer fully or partially inhibited melt crystallization, which for example can be achieved by fast cooling/quenching. The critical cooling rate for suppression of crystallization on cooling depends on the specific polymer, that is, the maximum crystallization rate. In case of the iPP homopolymer, it has been found that formation of crystals during cooling can be suppressed on cooling the liquid material at a rate faster than about  $100\text{ K s}^{-1}$  [30–33], while the critical cooling rate for suppression of crystallization is slightly lower in its random copolymers with 1-butene or ethylene [14,34,35]. Cooling the quiescent liquid at a rate between about 100 and  $1000\text{ K s}^{-1}$  allows development of a mesophase at about ambient temperature, which can be transferred into

crystals by subsequent heating [36–38]. At present, crystals of iPP-But random copolymers formed by quenching the quiescent liquid to ambient temperature and subsequent heating have been characterized with respect to their shape/habit, higher-order organization and selected engineering properties [39,40]. In short, semicrystalline iPP-But samples, prepared by cold crystallization via quenching and subsequent annealing at elevated temperature, contain spatially non-organized and non-lamellar crystals, which ultimately allows generation of optically highly transparent films of high modulus of elasticity [39,40], similar as has been proven for the iPP homopolymer [41,42].

To the best of our knowledge, there exist no studies about the internal structure of crystals of iPP-But random copolymers crystallized via the mesophase, which is therefore primary object of the present investigation. We believe that the evaluation of the effect of selection of a specific pathway of crystallization on the crystal structure is required for full characterization of the crystallization behavior of iPP-But random copolymers, in order to derive conclusions whether inclusion/exclusion of co-units into/from the crystalline phase is kinetically controlled. Finally, the investigation of the structure of samples crystallized via the mesophase, that is, by quenching the melt and subsequent annealing, we consider as relevant since rapid cooling of the melt is a typical element of polymer processing of this important class of polymeric materials.

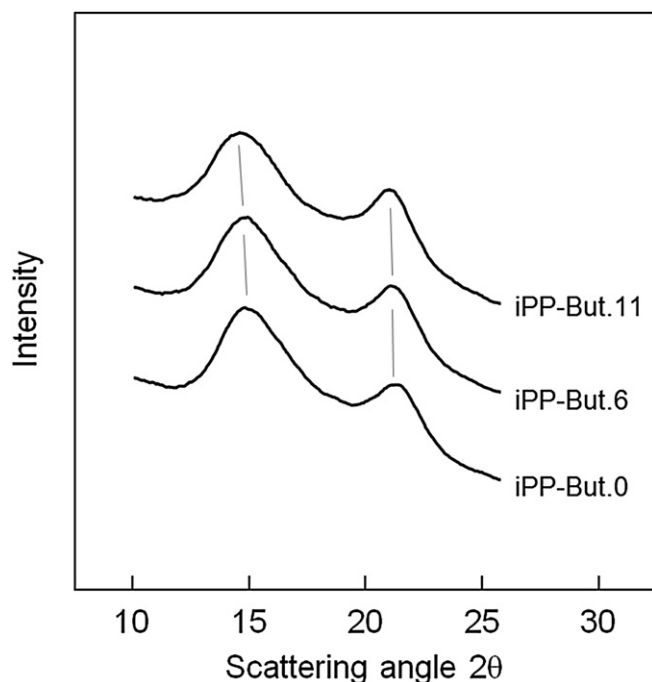
## 2. Experimental section

### 2.1. Materials

Isotactic poly(propylene-*ran*-1-butene) samples with a concentration of 6.0 and 10.9 mol-% 1-butene (iPP-But.6 and iPP-But.11) were purchased from Sigma–Aldrich [43]. The mass-average molar mass and polydispersity were 225 kDa and 3.1, respectively [44]. The iPP homopolymer with a molar mass and polydispersity of 373 kDa and 6.2, respectively, was provided by Montell Polyolefins [45]. The as-received materials were processed to films of thickness of about  $100\text{ }\mu\text{m}$  between Teflon sheets by compression molding at 473 K using a Perkin–Elmer FTIR press in combination with a LOT-Oriel die and temperature controller. Films were quenched in ice-water to obtain specimens of semimesomorphic structure. In situ X-ray analyses of changes of structure during heating and annealing of initially quenched samples were performed using the specific instrumentation at HasyLab, as described below. Alternatively, reorganization of the structure of quenched samples was performed by inserting specimens in a pre-heated Heraeus oven, annealing for a period of 60 min, and ballistic re-cooling to ambient temperature, by removing the film from the oven.

### 2.2. Instrumentation

Wide-angle X-ray scattering (WAXS) experiments were performed to gain information about the structure of the mesophase, the transition from the semimesomorphic structure into semi-crystalline structure, the  $\alpha/\gamma$  polymorphism, and the dimensions of the unit cell of the crystal phase formed by cold crystallization. WAXS analyses were performed on a diffractometer URD 63 from Seifert-FPM, which was operated in transmission mode. We used Ni-filtered  $\text{CuK}\alpha$ -radiation with a wavelength of 0.15418 nm and a scintillation counter for registration. In order to increase the signal-to-background ratio, several films of the polymer were stacked to increase the irradiated volume. Diffractometer experiments, throughout, were performed at ambient temperature. For final calibration of the scattering angle, we employed  $\text{CaF}_2$  powder which exhibits a strong reflection at  $28.288\text{ deg}$  ( $2\theta$ ), when using  $\text{CuK}\alpha$  radiation.



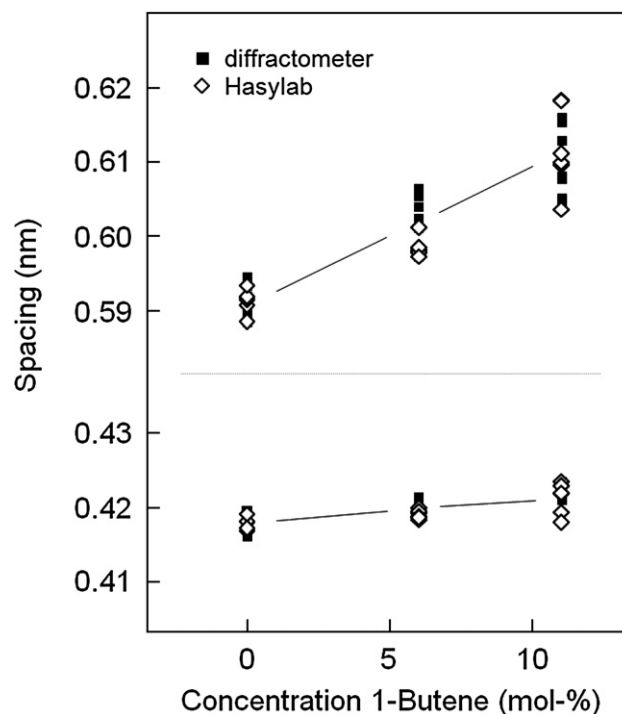
**Fig. 1.** WAXS diffractometer scans of quenched samples of the iPP homopolymer (iPP-But.0) and random copolymers of propylene and 1-butene with 6 and 11 mol-% 1-butene (iPP-But.6 and iPP-But.11).

Temperature-resolved WAXS experiments were performed at the A2 beamline at HASYLAB (Germany). The wavelength of the radiation and the sample–detector distance were 0.15 nm and about 106 mm, respectively. Scattering data were collected in transmission mode using a two-dimensional MarCCD165 detector. Several layers of the 100 μm polymer film were carefully stacked, wrapped into aluminum foil, and placed in a temperature-controlled sample holder. The normal of the sample film was oriented parallel to the beam with a size of approximately 2 mm (vertical direction) × 3 mm (horizontal direction). Typically, the accumulation time to obtain an X-ray frame was 20 s. Initially quenched and therefore semi-mesomorphic samples were heated in vacuum atmosphere at a rate of 2 K min<sup>-1</sup>. With an accumulation time of 20 s per frame and a readout/dead time of the detector of less than 10 s, one frame per kelvin temperature change is observed.

Supplemental differential scanning calorimetry (DSC) data have been collected using a power-compensation instrument DSC 7 from Perkin–Elmer. The device was operated in conjunction with the liquid nitrogen cooling accessory to ensure constant subambient temperature of the heat sink, while the furnaces were purged with dry nitrogen. The sample mass and the heating rate applied for analysis of structure reorganization on heating the semimesomorphic preparations were about 5 mg and 20 K min<sup>-1</sup>, respectively.

### 3. Results and discussion

Fig. 1 shows WAXS diffractometer scans of quenched samples of the iPP homopolymer (bottom curve) and iPP-But random copolymers with 6 and 11 mol-% 1-butene (center and top curves). The observed scattering patterns are typical for semimesomorphic samples which consist of an amorphous phase and a mesophase [26,36–38,46–50]. The two halos at about 15 and 21 deg (2θ) correspond to distances of about 0.59 and close to 0.42 nm within the mesophase, respectively. Axial deformation of quenched iPP allowed to observe fiber pattern, with the first and second halo

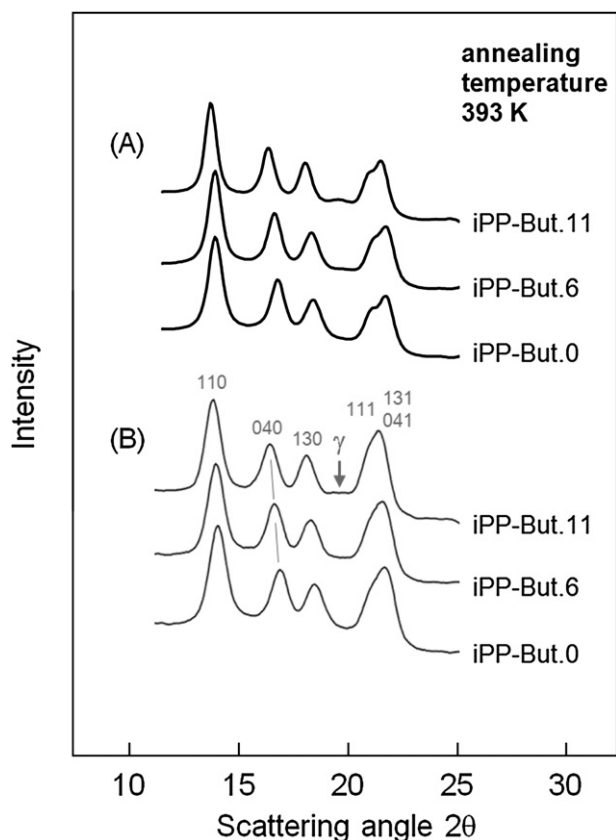


**Fig. 2.** Spacings in the mesophase of quenched samples of iPP-But random copolymers as a function of concentration on 1-butene. The distances of 0.59 nm and close to 0.42 nm at zero concentration of 1-butene are related to inter- and intramolecular repeats, respectively.

located at the 0th and 1st layer line [50,51]. Consequently, it was concluded that the first halo at 0.59 nm corresponds to the distance between chains while the second halo at a layer line spacing of 0.65 nm is related to the intramolecular helical repeat. From the raw data of Fig. 1 it can be seen that addition of 1-butene co-units results in a shift of both halos towards lower scattering angles, as is indicated with the thin lines connecting the maxima of the curves. Moreover, the shift of the halo at about 15 deg (2θ) is considerably larger than that of the halo at about 21 deg (2θ).

Quantitative data about inter- and intramolecular spacings in the mesophase of quenched iPP-But random copolymers are shown in Fig. 2 as a function of the concentration on 1-butene. The open and filled symbols represent data which were obtained by different experimental setups, as is indicated in the legend. While the intramolecular spacing of about 0.42 nm is only weakly affected by addition of 1-butene co-units in the chain, the intermolecular distance of 0.59 nm in the homopolymer is strongly increased in samples containing 6 and 11 mol-% 1-butene. Obviously, during quenching the quiescent liquid of a homogenous mixture of propylene and 1-butene units, the latter are incorporated in the mesophase of polypropylene and cause a change of the average distance between molecular stems. The linear increase of the interchain distance with increasing 1-butene concentration, at least in the investigated range up to 11 mol-% 1-butene, indicates that the 1-butene content in the mesophase is strictly proportional to the overall concentration of co-units in the chain. It is therefore assumed that the 1-butene concentration in the mesophase is identical to that in the liquid state/surrounding amorphous structure.

The increase of the distance between molecular stems with increasing content of co-units can be recalculated into a decrease of the density of the mesophase. According to the data of Fig. 2, the density of the mesophase decreases by about 0.5–0.6% per addition of 1 mol-% 1-butene co-units, which is in qualitative though not quantitative agreement with macroscopic density data, published



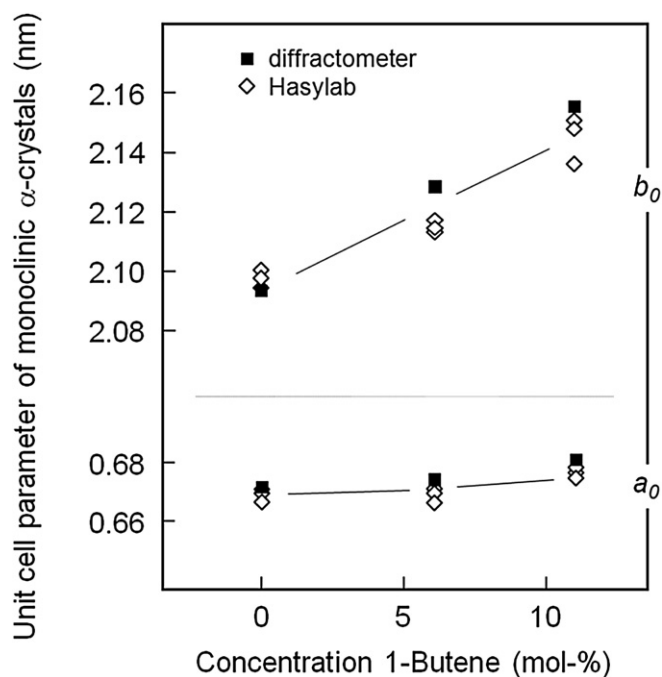
**Fig. 3.** WAXS diffractometer scans of initially quenched and subsequently at 393 K cold-crystallized samples of the iPP homopolymer (iPP-But.0) and random copolymers of propylene and 1-butene with 6 and 11 mol-% 1-butene (iPP-But.6 and iPP-But.11). (A) HasyLab data: approach of annealing temperature at  $2 \text{ K min}^{-1}$ ; annealing time 30 min; re-cooling to ambient temperature at  $10 \text{ K min}^{-1}$ . (B) diffractometer data: ballistic approach of the annealing temperature by temperature jump; annealing time 60 min; ballistic re-cooling to ambient temperature.

recently (Figs. 4 and 5 in [14]). The observed decrease of the macroscopic density with increasing content of 1-butene in this former study is distinctly lower than expected from the reduction of the density of the mesophase. However, a quantitative discussion of the macroscopic density at least requires information about the mesophase content and the density of the amorphous phase. At present both of these are not available. Note that the density of the amorphous phase may slightly be increased due to the presence of 1-butene co-units in the copolymer, as can be concluded from pVT data of both constituents [52].

Fig. 3 is a plot of azimuthally averaged WAXS HasyLab data (A) and of WAXS diffractometer scans (B), obtained on sets of samples which initially were quenched, to allow mesophase formation, and subsequently annealed at a temperature of 393 K, to convert the semimesomorphous into a semicrystalline structure. The exact conditions of annealing including the approach of the annealing temperature, the annealing time, and the rate of final cooling to ambient temperature were slightly different, however, and as expected, did not affect the final structure. The WAXS data of Fig. 3 clearly confirm the transition from the semimesomorphous state (see Fig. 1) into a semicrystalline state of structure. All samples — after annealing at 393 K — mainly contain monoclinic  $\alpha$ -crystals while the orthorhombic  $\gamma$ -modification barely is observed. Negligible amount of  $\gamma$ -phase has only been developed in the sample iPP-But.11, as is indicated with the arrow at the position of the characteristic 117  $\gamma$ -peak [27]. The almost complete absence of  $\gamma$ -crystal

formation is expected since it is typically found only as a result of a specific mechanism of growth and branching of lamellae which in samples crystallized via the mesophase, as in the present study, is not evident. In random iPP-But copolymers with a concentration of 1-butene of less than 10 mol-%, appreciable amount of  $\gamma$ -phase has only been detected if the crystallization was performed at temperatures higher than about 330–340 K [8]. The mesophase, in contrast, is formed at temperatures below about 320–330 K [33]. Due to the high nucleation density, lateral growth of the ordered domains/mesophase to yield lamellae able to branch, is restricted. There is evidence, based on experimental data [31,37,53–56], that subsequent reorganization of the structure by heating and isothermal annealing is not connected with formation, growth and branching of lamellae. However, the minor amount of  $\gamma$ -crystals on heating of initially semimesomorphous random iPP-But copolymers may be related to partial transformation of supercooled liquid into crystals. It is assumed that the mesophase – crystal phase transition, which occurs in a wide temperature range within the existing domains, is connected with release of strain of amorphous segments located near the crystal boundaries which then may epitaxially crystallize on existing surfaces. It can therefore be speculated that the observation of  $\gamma$ -crystals in initially quenched and subsequently re-crystallized iPP-But random copolymers indicates a phase transformation of supercooled liquid into crystals.

Beside the observation of formation of only minor amount of  $\gamma$ -crystals on cold crystallization of semimesomorphous polypropylenes, the data of Fig. 3 reveal distinct expansion of the unit cell of the monoclinic  $\alpha$ -crystals. The positions of the crystalline peaks are shifted toward lower scattering angle on addition of 1-butene co-units which is indicated in the lower set of curves of Fig. 3 with the vertical line connecting the 040 peaks. The 040 peak has been used to calculate the dimension of the monoclinic unit cell in direction of the  $b$ -axis while the 110 and 130 peaks were employed to get information about the unit cell dimension in direction of the  $a$ -axis. Fig. 4 shows the unit cell parameters  $a_0$  and  $b_0$  of the monoclinic unit cell as a function of the concentration on



**Fig. 4.** Unit cell parameters  $a_0$  (bottom data) and  $b_0$  (top data) of monoclinic  $\alpha$ -crystals, formed on heating semimesomorphous structure, as a function of the concentration of 1-butene.

1-butene co-units. It can be seen that the unit cell mainly is expanded in direction of the  $b$ -axis while the dilation is negligible in direction of the  $a$ -axis. Almost identical results regarding the increase of the  $b_0$  parameter of the monoclinic unit cell were obtained on random iPP-But copolymers which have been crystallized at qualitatively different conditions [3,7,8,11,13], for example, by direct transformation of liquid structure at low supercooling, by crystallization during polymerization, or by crystallization from solution. We conclude therefore that the incorporation of 1-butene co-units into the monoclinic crystal lattice is not primarily controlled by the exact pathway of crystallization, which may perhaps be due to the relative low increase of the free enthalpy of the crystals on incorporation of 1-butene co-units — as has been proven by molecular modeling [7] — in relation to a relative high energy barrier required for repulsion of co-units during the crystallization process.

It is furthermore emphasized that the expansion of the monoclinic unit cell of iPP due to presence of constitutional 1-butene chain defects ultimately, that is, at high concentration of 1-butene, does not lead to the structure of form I crystals of isotactic poly(1-butene) (iPB). Though there is observed co-crystallization at all concentrations of propylene or 1-butene in the chain [3], the crystal structures of iPP containing 1-butene co-units, and of iPB containing propylene units remain different, that is, Vegard's rule [57] cannot be applied to describe the change of the crystal structure as a function of the concentration of co-units in the entire concentration range. The phase inversion occurs at a concentration of about 50 m-% 1-butene [3].

The inclusion of 1-butene co-units in the mesophase and in subsequently formed crystals is expected for kinetic reasons. If there would be required exclusion of co-units due to energetic/thermodynamic reasons — which seems not true for random iPP-But copolymers — then, most likely, it would occur on slow crystallization. Any selection/segregation of crystallizable segments at the crystal growth front needs time for diffusion, and is therefore best completed on slow crystallization, that is, on isothermal crystallization at low supercooling, or on slow cooling. In contrast, the selection process of crystallizable sequences gets increasingly imperfect with the crystallization performed at high supercooling or at fast cooling of the melt; in simple words, chain defects are then trapped into the crystalline phase. The effect of cooling rate on crystallization, for example, has been evaluated for the specific case of random copolymers of ethylene and 1-octene. It has been demonstrated that slow cooling resulted in formation of orthorhombic crystals as in the polyethylene homopolymer while fast cooling increasingly disabled exclusion of the hexyl branches from the crystal lattice, ultimately resulting in formation of less ordered pseudo-hexagonal crystals [58–60]. For the random copolymers of propylene and 1-butene of the present study it is straightforward to expect that quenching the melt and mesophase formation at ambient temperature is connected with inclusion of 1-butene units since these co-units are even included on slow crystallization at low supercooling.

Further evidence for absence of  $\gamma$ -crystal formation and expansion of the monoclinic unit cell of crystals in random iPP-But copolymers crystallized via the mesophase has been gained by in situ measurement of the reorganization of structure during heating. Fig. 5 shows temperature-resolved WAXS data of the iPP homopolymer (bottom data set) and of the iPP-But random copolymers with 6 and 11 mol-% 1-butene (center and top data sets, respectively), recorded during continuous heating at  $2 \text{ K min}^{-1}$ . The front curve in each data set was measured at a temperature of 303 K, and proves presence of mesophase after quenching. The final curve in each data set was recorded at 383 K and indicates presence of monoclinic structure, that is, the temperature range monitored included the onset of the transition from the semimesomorphous to the semicrystalline structure.

Qualitative inspection of the data reveals no difference between the investigated polymers regarding the change of structure on heating; there is no indication of formation of  $\gamma$ -structure in any of the samples, and the mesophase – crystal phase transition seems to occur in a similar range of temperatures in the various polymers. Quantitative evaluation of data yields some further information.

Fig. 6 is an enlargement of the WAXS data of Fig. 5 showing in detail the scattering intensity in the angular range of the 110 peak of the monoclinic  $\alpha$ -phase. The individual curves, which were recorded as a function of temperature, are not staggered along the  $x$ - and  $y$ -axes as in Fig. 5, and allow therefore easy comparison of the peak positions from both the mesophase halo and the 110 peak of the  $\alpha$ -phase before and after the structure reorganization. The vertical lines in Fig. 6 are included to guide the eye and need to be read from bottom to top in order to recognize the effect of increasing concentration of 1-butene on the mesophase halo (right lines) and 110  $\alpha$ -phase peak (left lines). It can clearly be seen that both maxima are shifted to lower scattering angle on increasing 1-butene content, confirming the data of Figs. 1 to 4 which are based on independent experiments. Next, the evolution of the intensity of the monoclinic  $\alpha$ -crystal peak with increasing temperature was analyzed, in order to obtain information whether the presence of 1-butene affects the transition from the semimesomorphous into the semicrystalline structure.

Fig. 7 shows the intensity of the 110 peak of monoclinic  $\alpha$ -crystals of the various polymers as a function of temperature, based on the

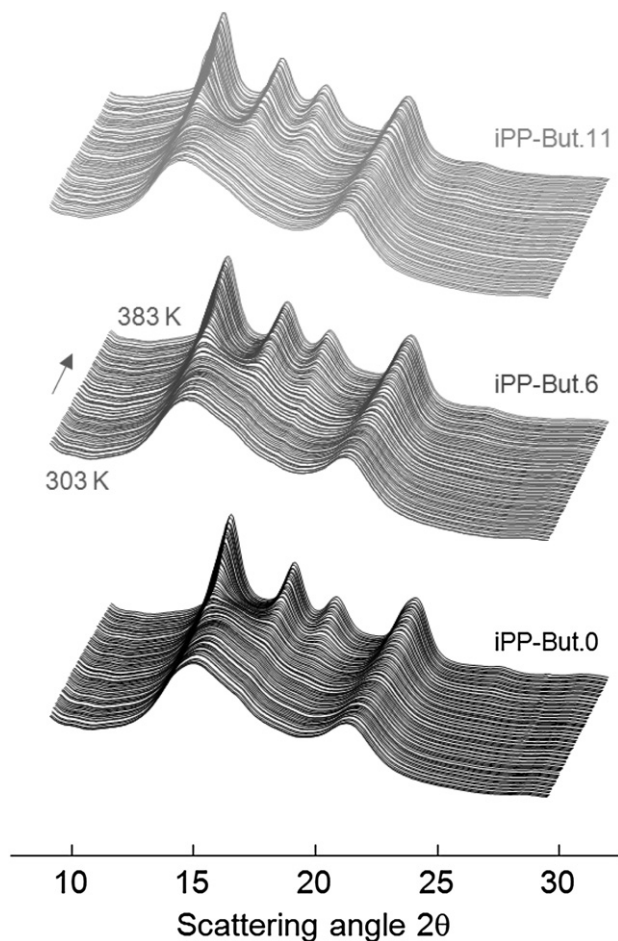
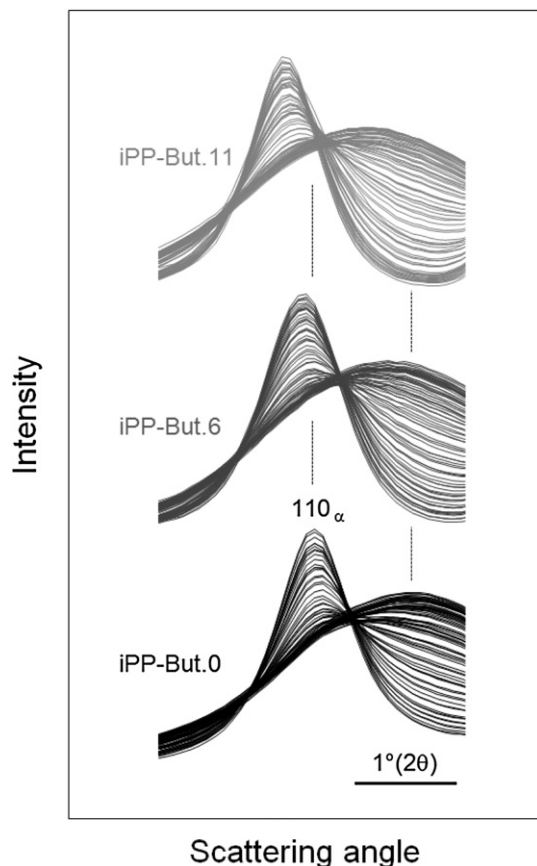


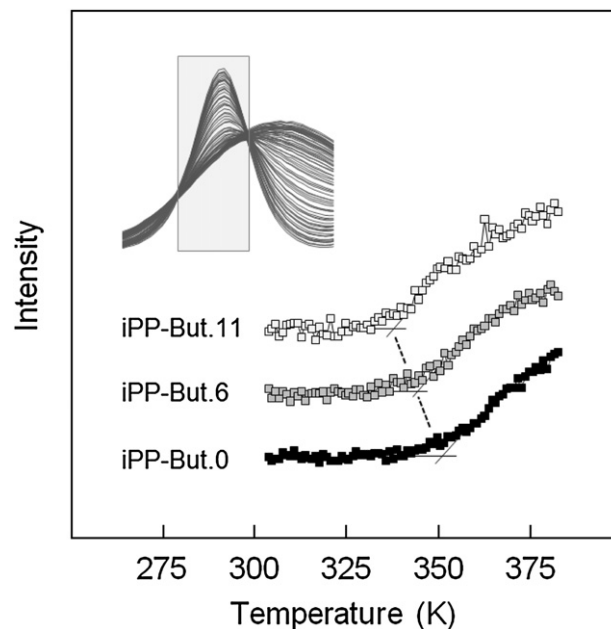
Fig. 5. WAXS of iPP-But random copolymers with 0 (bottom), 6 (center), and 11 mol-% 1-butene (top), recorded as a function of temperature during continuous heating at  $2 \text{ K min}^{-1}$  between 303 K (front curve) and 383 K (final curve).



**Fig. 6.** WAXS of iPP-But random copolymers with 0 (bottom), 6 (center), and 11 mol-% 1-butene (top) in the angular range of the 110 peak of the monoclinic  $\alpha$ -phase, recorded as a function of temperature during continuous heating at  $2 \text{ K min}^{-1}$  between 303 and 383 K.

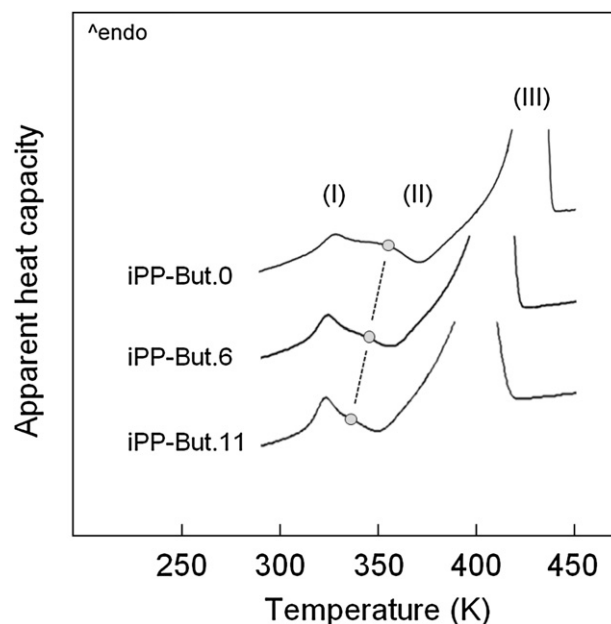
data shown in Figs. 5 and 6. The data sets are vertically shifted for clarity, with the first data points representing zero intensity since the quenched samples do not contain crystals at ambient temperature. In the top part of Fig. 7, temperature-resolved scattering curves of the sample iPP-But.6 are shown for demonstration of the calculation of the temperature dependence of the relative content of  $\alpha$ -crystals. First, the relative intensity of each scattering curve including the angular range of the 110 peak of the  $\alpha$ -phase was integrated between the  $2\theta$ -limits indicated with the gray box, and then from each integral-intensity value that of the first curve, recorded at 303 K, was subtracted. We are aware that this procedure does not yield absolute values of the crystallinity; however, we consider it as an effective scheme for evaluation of the evolution of the crystalline content as a function of temperature.

The data of Fig. 7 reveal that monoclinic crystals are detected at lower temperature on continuous heating of semimesomorphous samples if 1-butene co-units are present. There is observed a systematic trend which is indicated in Fig. 7 with the dashed line connecting the onset temperatures of detection of monoclinic crystals. The decrease of the onset temperature of detection of monoclinic crystals on heating initially semimesomorphous samples — as detected by WAXS — is about 6 and 12 K in the iPP-But random copolymers with 6 and 11 mol-% 1-butene, respectively. This observation is confirmed by calorimetric investigation of the thermal behavior of initially quenched iPP-But random copolymers. Fig. 8 shows apparent specific heat capacity data of initially semimesomorphous samples of different concentration of 1-butene as a function of temperature. The heating scans show an endothermic



**Fig. 7.** Intensity of the 110 peak of the monoclinic  $\alpha$ -phase of iPP-But random copolymers with 0 (bottom), 6 (center), and 11 mol-% 1-butene (top) as a function of temperature. The data sets related to the various polymers are vertically shifted for clarity. The calculation is based on the integration of the peak intensity, with the integration limits sketched in the top part of the Figure.

annealing peak (I), an exothermic reorganization/cold-crystallization peak (II), and final melting (III). The peak and onset temperatures of the annealing peak are nearly independent on the concentration of 1-butene and are about 325 K and 310 K, respectively. This result, that is, the independence of the temperature of the annealing peak on the concentration of 1-butene is expected since it depends primarily on the annealing temperature which was



**Fig. 8.** Apparent heat capacity of iPP-But random copolymers with 0 (top), 6 (center), and 11 mol-% 1-butene (bottom) as a function of temperature, measured on continuous heating at  $10 \text{ K min}^{-1}$ . The data were collected in order to prove an effect of presence of 1-butene co-units on the temperature of structure reorganization of initially semimesomorphous preparations.

identical for the various polymers of this study. In contrast, the temperature range of the exothermic event (II) decreases systematically with increasing concentration of 1-butene, similar as has been observed by temperature-resolved WAXS. The exothermic peak (II) mainly is due to transformation of the mesophase into the monoclinic structure, although a minor contribution due to transformation of supercooled liquid into monoclinic crystals is possible, that is, classical cold crystallization cannot be fully excluded. The approximate start of the exothermic reorganization is indicated with the gray circles in Fig. 8 while the dashed lines between the individual curves help to recognize the effect of concentration of 1-butene co-units on the onset temperature of the particular transition. As expected, the temperature of first observation of monoclinic crystals by temperature-resolved WAXS (Fig. 7), and the onset temperature of the exothermic peak in the DSC data agree on an absolute scale (Fig. 8). The decrease of the temperature of first detection of monoclinic crystals, observed by WAXS, and of the temperature range of exothermic reorganization, measured by DSC, with increasing concentration on 1-butene can be explained with a shift of the glass transition temperature of the mesophase toward lower temperature, as described below.

The mesophase of iPP has been classified as a conformationally disordered glass (CD glass) [61,62], based on a quantitative analysis of the temperature dependence of the apparent specific heat capacity of iPP of different thermal history [62–64]. The CD glass of iPP starts to transform on slow heating into monoclinic crystals at a temperature of about 350–360 K when the helix mobility within the mesophase allows the removal of helix reversals [65]. It is emphasized that the annealing peak observed at about 305–320 K reflects the thermal/thermodynamic stability of the mesophase initially grown at the temperature of the coolant during quenching (273 K), and subsequently annealed at ambient temperature (between about 291 and 295 K). Slow heating below 350 K results in steady increase of order in the mesophase, which ultimately converts into crystalline structure at about 350–360 K. These reorganization processes within the mesophase domains are also affected by an increasing mobility of the surrounding amorphous phase with increasing temperature, and, correspondingly, increasing mobility of molecular segments in the mesophase. It is evidenced that the mesophase of iPP is surrounded by a so-called rigid amorphous fraction (RAF) which, in case of partially ordered polymers, is due to restraint of the mobility of the amorphous phase by covalent coupling to crystals/ordered domains [66–69]. The RAF surrounding the mesophase of iPP has a broad glass transition which ultimately also affects the mobility of segments in the mesophase. The upper limit of the glass transition of the RAF of the mesophase, and also of the glass transition of the CD mesophase is about 350–360 K in case of the iPP homopolymer — coinciding with the onset of exothermic reorganization in DSC analysis and appearance of monoclinic peaks in temperature-resolved WAXS experiments.

In random iPP-But copolymers, the glass transition temperature of the unrestrained, mobile amorphous fraction (MAF) is lowered by about 5–10 K on addition of 10 mol-% 1-butene [8,70]. For example, the glass transition temperatures of random iPP-But copolymers have been measured by DSC on samples which were non-isothermally melt-crystallized at a rate of 10 K min<sup>-1</sup>, followed by ageing at room temperature [70]. In this particular study, a glass transition temperature of about 269 K was detected in case of the homopolymer, while the glass transition temperature was lowered by 7 K to 263 K in a random iPP-But copolymer containing 10 mol-% 1-butene. For the quenched semimesomorphous homopolymer and the two random copolymers of the present study with 6 and 11 mol-% 1-butene we detected DSC glass transition temperatures of about 276, 273, and 268 K, respectively. Though the glass transition temperature of the

MAF of quenched preparations seems few kelvin higher than that of semicrystalline preparations of identical chemical composition — as has recently been analyzed and interpreted in detail in terms of coupling of the amorphous and crystalline phases including the area of the crystalline–amorphous interface for the specific case of the iPP homopolymer [71] — we recognized a similar decrease of the glass transition temperature with increasing concentration on 1-butene as was observed in samples crystallized on rather slow cooling [8,70]. Note that an in-depth discussion of the change of the glass transition temperature on variation the concentration of 1-butene and thermal history of sample is beyond the scope of the present study and will be provided separately. As a matter of fact, we observed in the quenched preparations of this work a decrease of the glass transition temperature of the MAF which, we believe, affects also the properties of the RAF, spatially being located between the MAF and the mesophase/CD glass. It is straightforward to assume that the decrease of the glass transition temperature of the MAF leads to a decrease of the glass transition temperatures of both the RAF and the mesophase.

A further reason for the observed decrease of the temperature of first detection of monoclinic crystals by WAXS/exothermic reorganization by DSC in random iPP-But copolymers can be the lowered stability of the mesophase. The detected inclusion of 1-butene co-units in the mesophase (see Figs. 1 and 2) increases its free enthalpy and correspondingly increases the thermodynamic driving force towards the transition to the more stable monoclinic crystal phase. The inclusion of the copolymer units, thus, increases the mobility of the CD glass and the driving force toward the more stable phase. Not yet published experimental results [72] obtained by sufficiently fast scanning calorimetry, to bypass the mesophase — crystal transition, also indicate that the mesophase of random iPP-But copolymers is less stable. The zero-entropy-transition temperature, going directly from the mesophase to the supercooled liquid, occurs at lower temperature, indicating a lower thermodynamic stability.

#### 4. Conclusions

In this work the process of structure formation of isotactic copolymers of propylene and 1-butene when crystallized via intermediate formation of a metastable mesophase at ambient temperature and subsequent heating/annealing has been studied. This particular pathway of crystallization had not been explored before from point of view of the fine structure/defect concentration of crystals, the  $\alpha/\gamma$  polymorphism, and the kinetics of reorganization of the semimesomorphous into a semicrystalline structure. The fine structure of the quenched copolymers is altered such that 1-butene co-units are incorporated into the mesophase without change in concentration. Heating results in a conversion of the semimesomorphous structure into the semicrystalline structure at the glass transition of the mesophase [62]. The conversion includes a transition of the mesophase into crystals which occurs on a local scale by removal of conformational defects within the ordered phase [62,73], and not by any significant amount of transition of supercooled liquid structure into crystals. Crystals which develop on heating by reorganization of semimesomorphous structure are of monoclinic symmetry. The minor amount of orthorhombic  $\gamma$ -crystals detected may be related to insignificant amount of new crystallization of amorphous structure, likely due to absence of the specific branching mechanism of crystals required for  $\gamma$ -crystal development. Analysis of the morphology of crystals in iPP-But random copolymers, formed via the semimesomorphous state, revealed presence of non-lamellar crystals in a non-spherulitic environment, similar as in the iPP homopolymer [54,74]. The concentration of 1-butene constitutional defects in the monoclinic crystals is similar as in preparations which were crystallized along qualitatively different pathways. The concentration of 1-butene co-

units in the crystal phase increases linear with the total concentration, which strengthens the notion that there is equal partitioning of co-units between the crystalline and amorphous phases, at least in the concentration range investigated. The transition of semi-mesomorphic structure into semicrystalline structure occurs at lower temperature in presence of 1-butene, at least if temperatures are viewed on an absolute scale. It is assumed that this observation is related to the decrease of the glass transition temperature of the mesophase with increasing 1-butene concentration and is possibly enhanced by the decrease in thermodynamic stability of the mesophase. A decrease of the glass transition temperature of the mobile amorphous fraction/phase is well known, and has also been confirmed for the quenched samples of the present work. The decreased glass transition temperature of the amorphous phase in random iPP-But copolymers also affects the temperature dependence of the intramolecular interaction to the mesophase such that sufficient mobility for removal of helix defects is reached at lower temperature than in the mesophase of the iPP homopolymer.

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