

In situ X-ray analysis of mesophase formation in random copolymers of propylene and 1-butene

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Received: 26 February 2011 / Accepted: 11 April 2011 / Published online: 19 April 2011
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Abstract The solidification of random isotactic copolymers of propylene and 1-butene has been followed in real time by wide-angle X-ray scattering as a function of the rate of cooling the quiescent liquid. The experimental setup allowed simultaneous recording of cooling curves—sample temperature as a function of time—and X-ray patterns at high sampling rate of 20 Hz. This approach allowed establishing a correlation between cooling rate, temperature of crystallization/mesophase formation, and X-ray structure, which formerly has only been observed *ex situ*, after completion of structure formation during cooling and subsequent aging. It is quantitatively confirmed that addition of 1-butene co-units into the propylene chain allows mesophase formation on cooling the melt at distinctly lower rate than in case of the homopolymer. The experimental results are compiled into a continuous cooling transformation (CCT) diagram and compared with data obtained earlier on random copolymers of propylene with ethylene.

Keywords Poly(propylene-ran-1-butene) · Crystallization · Mesophase formation

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Introduction

Isotactic polypropylene (iPP) belongs to the group of semicrystalline polymers in which the phase structure at ambient temperature is strongly controlled by the pathway of solidification [1, 2]. Slow cooling of the quiescent melt at a rate lower than about 10^2 K s^{-1} , or crystallization at low supercooling, leads to formation of monoclinic α -crystals of lamellar morphology and the development of a spherulitic superstructure. Cooling faster than about 10^2 K s^{-1} suppresses crystallization. Instead, if the cooling rate is lower than 10^3 K s^{-1} , a thermodynamically unstable mesophase forms at high supercooling with the maximum rate of mesophase formation being observed around ambient temperature [3–5]. The mesophase that has been identified as a conformationally disordered glass [6–8] is of nodular geometry and does not form a higher order superstructure [9–11]. Starting at about 350 K, it transforms on heating above its glass transition temperature into monoclinic structure by removal of conformational defects within the ordered domains [8, 12–15]. The crystallization of the mesophase is not connected with a change of the habit of the ordered phase and of the superstructure [16, 17]. Cooling the melt faster than 10^3 K s^{-1} below the glass transition temperature of 270 K, finally, leads to suppression of both crystallization and mesophase formation [5]. However, depending on the heating rate, cold-ordering and/or cold-crystallization may occur on subsequent devitrification of the amorphous glass [10, 18]. In summary, variation of the pathway of solidification the quiescent melt of iPP permits generation of qualitatively different structures, which, for example, can advantageously be used to tailor properties and to widen fields of application of iPP [19, 20].

The kinetics of crystallization and mesophase formation, the physical structure, and ultimate properties of iPP, furthermore, are effectively controlled by the chemical architecture of the macromolecule. A common route to modify the chain structure is the random copolymerization of propylene with low amount of 1-butene. The 1-butene co-units shorten the isotactic sequences of propylene and disturb therefore the ordering process on solidification the quiescent melt. Former research on structure formation of poly(propylene-*ran*-1-butene) included the analysis of the partitioning of 1-butene co-units between the crystalline and amorphous phases, analysis of the α/γ crystal polymorphism and change of the crystallization kinetics, or the evaluation of the crystal geometry and spherulitic superstructure [21–32]. In short, 1-butene co-units enter the crystalline phase of iPP and favor additional formation of γ -crystals with the ratio between α - and γ -crystals increasing with decreasing crystallization temperature. The crystallization temperature, measured on continuous cooling, and the isothermally measured crystallization rate decrease with increasing concentration of 1-butene in the chain. Furthermore, it has also been recognized that the change of the crystallization behavior due to the presence of 1-butene is less than in case of random copolymers of propylene with ethylene, 1-hexene, or 1-octene, mainly due to the relative ease of incorporation of 1-butene co-units in the crystalline phase, as is judged from molecular-modeling results [27].

The majority of investigations on structure formation of poly(propylene-*ran*-1-butene) focused on crystallization at low supercooling. Though it has been

found—similar as in case of the homopolymer—that crystals are replaced by mesophase on increasing the cooling rate on solidification of the melt [30–32], there is still lack of knowledge about the exact conditions of formation the different phases. These information, however, are required for further understanding the polymorphism in polymers and to provide guidelines for generation specific semimesomorphic or semicrystalline polypropylene-based structures. In an initial study about the kinetics of structure formation of poly(propylene-*ran*-1-butene), using fast scanning chip calorimetry (FSC), we analyzed the temperature of crystallization and/or temperature of mesophase formation as a function of the rate of linear cooling [33]. Most important in the context of the present work, crystallization/mesophase formation has only been detected on cooling slower than about 10^2 K s^{-1} in the specific case of a copolymer containing 11 mol.% 1-butene. The critical cooling rate for complete suppression of ordering of 10^2 K s^{-1} in poly(propylene-*ran*-1-butene) with 11 mol.% 1-butene is therefore distinctly lower than in case of the iPP homopolymer. Unfortunately, based on the analysis of the crystallization/ordering temperature, it was not possible to distinguish between crystallization and mesophase formation, preventing a precise forecast of structures forming at rapid cooling. In order to achieve this goal, we employed in this work a new experimental technique which allows simultaneous recording of cooling curves, sample temperature as a function of time, and collection of wide-angle X-ray scattering patterns. This technique allows the detection of transition temperatures as a function of cooling rate and additionally provides information about the polymorph formed during the cooling step of the experiment. Since the instrumentation is optimized for analysis of structure formation at fast cooling, this approach can be considered as an extremely useful addendum to the FSC technique, which allows measurement of the temperature and heat of transitions, however, which cannot provide structural information.

Experimental

Materials and sample preparation

Samples of isotactic poly(propylene-*ran*-1-butene) with a concentration of 6.0 and 10.9 mol.% 1-butene, a molar mass of 225 kDa, and polydispersity of 3.1 (Private communication, Linz, Borealis, 2008) were obtained from Sigma-Aldrich (Munich, Germany). In the following, the copolymers containing 6.0 and 10.9 mol.% 1-butene are labeled iPP-But.6 and iPP-But.11, respectively. The as-received powders were compression molded at 473 K between Teflon sheets to films of about 100 μm thickness in a Perkin Elmer laboratory press, operated in conjunction with a Lot-Oriel heating device/die. In a further preparation step, the sample films were re-melted on a glass slide, using a hot stage, and folded around a Chromel–Alumel μ -thermocouple. As a result, films with an approximate thickness of 100–200 μm and area of $10 \times 20 \text{ mm}^2$ were obtained, with the thermocouple being located in the center layer of the specimens. Subsequently, the specimens were wrapped into

aluminum foil of 20 μm thickness and inserted into the sample holder, described below.

Instrumentation

The experiments for simultaneous observation of cooling curves and temperature-resolved wide-angle X-ray scattering (WAXS) data were performed at the BM26B-Dubbe beamline at ESRF, using monochromatic X-rays of wavelength of 0.124 nm and a Pilatus 300K-W detector for fast data collection. The measurements were performed in asymmetric transmission mode, that is, the large area of the sample was oriented perpendicular to the X-ray beam of approximate diameter of 300 μm . A typical temperature-resolved measurement included the collection of 600 WAXS frames at a frequency of 20 Hz, that is, each 50 ms (47 ms intensity accumulation and 3 ms detector readout) a new WAXS frame was acquired. The sample–detector distance was calibrated by the analysis of the position of scattering peaks of an iPP standard of high crystallinity, containing monoclinic α -crystals. Before further data processing and analysis, the two-dimensional X-ray frames were azimuthally averaged to obtain line scans, intensity versus scattering angle, of reasonably low noise. Regarding the temperature signal, the μ -thermocouple was connected to a fast data acquisition logger HP 34970A. To obtain a perfect correspondence between the sample temperature readout and WAXS frame, the X-ray beam was positioned at a distance of less than 500 μm from the thermocouple junction. Furthermore, the acquisition of the temperature signal was triggered by the WAXS detector. Heating and cooling of the sample were achieved by blowing hot or cold air tangentially and nearly perpendicular to the large surfaces of the film, respectively, using separate circuits for air supply. Typically, the samples of the present work were melted by heating to 453 K into the liquid state and kept at this temperature for a period of 3 min, before cooling. The cooling rate was manually adjusted by the flux of air of ambient temperature. The switch-over from blowing of hot air for heating and isotropization of the sample to blowing of cold air for cooling was remotely controlled such that acquisition of X-ray frames was allowed well before start of the cooling segment. At the end of the cooling experiment, when the sample reached the target ambient temperature, the structure was additionally investigated by collecting an X-ray pattern with an exposure time of 15 s. Further description of the experimental setup is available in recent reports about real time WAXS detection of mesophase development during quenching of random copolymers of propylene and ethylene [34], or about the observation of continuous cooling curves and their analysis for evaluation of the role of ethylene co-units in these copolymers [35].

In summary, samples of poly(propylene-*ran*-1-butene) were cooled from 453 K to ambient temperature at different rate while exposed to the X-ray beam for quasi-continuous recording of WAXS frames at a frequency of 20 Hz. The read-out of the thermocouple is used to obtain cooling curves—sample temperature as a function of time. The cooling curves provide information about the cooling rate adjusted by the flux of air and about the temperature of the transformation of the liquid phase to either crystals or mesophase. The phase transformation is connected with the release of latent heat which causes a deviation from the exponential decrease of the sample

temperature with increasing time. As such, the cooling curves yield the relationship between the temperature of the crystallization or mesophase formation and the cooling rate. In addition, the temperature of the phase transition is also reliably detected by analysis of the X-ray patterns. The true advance of the quasi-continuous recording of the WAXS data as a function of temperature, however, is the gain of knowledge about the polymorph/structure formed at a certain temperature as a result of a specific cooling process.

Results and discussion

Cooling curves

Figure 1 shows cooling curves, sample temperature as a function of time, obtained on iPP-But.6 (a) and iPP-But.11 (b). The different curves in each plot represent experiments in which the cooling rate was varied by adjustment of the flux of air blown to the surface of the sample. The curves approach ambient temperature according to Newton's law of cooling [36]. It predicts an exponential decrease of the temperature, with the time constant in the experiments of this study controlled by the flux of air used for cooling. Furthermore, it is obvious that the cooling rate is not constant rather than decreases with decreasing temperature. However, since it is the intention of the present work to establish a relationship between cooling rate and both temperature of ordering and the polymorph formed, a reference-cooling rate needs to be defined for benchmarking and comparison of results. In this work, we adopt the approach of Piccarolo, who suggested in his early pioneering work about structure formation of iPP on rapid cooling [3] to employ the cooling rate observed at the temperature of the maximum crystallization rate of iPP of 343 K. Accordingly, the cooling experiments on iPP-But.6, shown in Fig. 1a, were performed at rates of about 1, 5, 7, 13, 34, and 67 K s⁻¹. In case of the cooling experiments on iPP-But.11, shown in Fig. 1b, the cooling rates at 343 K were 1, 2, 4, 12, 20, 29, 39, 50, and 68 K s⁻¹. It is known from earlier work on crystallization and mesophase formation of iPP that the selected range of cooling rates covers the transition from crystallization at low rate to mesophase formation at higher rate [3–5, 32, 33, 35], being important to achieve the goal of this work.

In general, the exponential approach of the target ambient temperature is delayed in case of the occurrence of a first-order phase transition within the sample, being connected with the evolution of heat. Depending on the amount of heat generated in the sample, there may not only be observed a slowing down of the decrease of the temperature rather than the measured temperature may be constant for a certain period of time or even may increase due to the phase transition. In Fig. 1a and b, the onset of the liquid–crystal or liquid–mesophase transition, as judged by eye, is indicated with the circles. The temperature of the phase transition decreases with increasing cooling rate which is expected from the crystallization theory [37, 38]; a review about the theoretical background and approaches of quantitative modeling of the cooling-rate dependence of crystallization is available in the literature [39] and is not repeated at this occasion. Furthermore, it is observed that the time required to

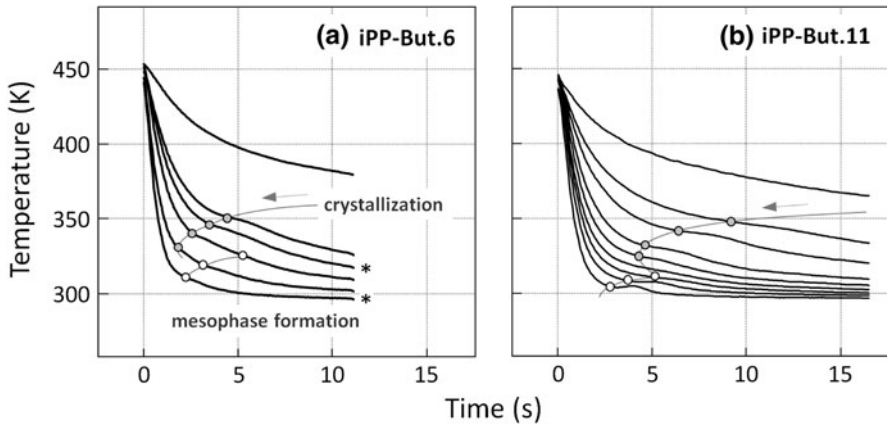


Fig. 1 Sample temperature as a function of time, obtained on cooling iPP-But.6 (a) and iPP-But.11 (b) at different rates. The *gray and white circles* indicate the temperature and time of crystallization and mesophase formation, respectively, as described in the text

initiate the crystallization process depends on temperature. The (gross) crystallization rate first increases and then decreases with increasing supercooling/decreasing temperature, as it is a consequence of the balance between the thermodynamic driving force for the phase transformation and mobility of chain segments required for diffusion [37, 38]. Accordingly, in the plots of the cooling curves in Fig. 1a and b, a characteristic nose is observed when the transition temperatures in the various cooling experiments are connected, yielding a phase transition line. With decreasing temperature, at first, and as is indicated by the arrows, the time at which crystallization occurs decreases, and then the time increases again due to the lowered mobility of chain segments. It is obvious from visual inspection of the raw data in Fig. 1 that two ordering processes of different kinetics are detected, presumably indicating formation of monoclinic α -crystals at high temperature (gray circles) and formation of mesophase at low temperature (white circles). Moreover, comparing the transition temperatures and times of the two copolymers of different 1-butene content, there is observed a distinct decrease of the temperature and increase of the time of crystallization with increasing concentration on 1-butene. For example, crystallization at 350 K occurs after 5 s in case of iPP-But.6, while the time required to initiate crystallization is almost doubled to 10 s in case of iPP-But.11 at identical temperature. This observation is linked to the decrease of both the equilibrium melting temperature and maximum crystallization rate with increasing concentration of 1-butene. Roughly, the decrease of the equilibrium melting temperature shifts the temperature range of crystallization to lower values, while the decrease of the maximum crystallization rate shifts the nose of the transition line to longer time. Regarding the effect of the concentration of 1-butene on the kinetics of the mesophase formation, unfortunately, based on the experiments of this study, firm conclusions cannot be drawn due to the limited number of data points. However, FSC experiments performed on identical copolymers revealed that

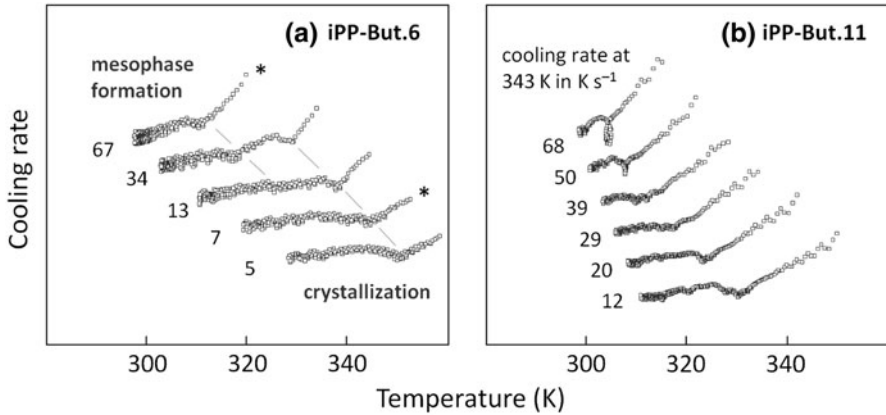


Fig. 2 Cooling rate as a function of the sample temperature for selected cooling experiments on iPP-But.6 (a) and iPP-But.11 (b). The curves are vertically shifted for the sake of clear presentation of the decrease of the temperature of the phase transition with increasing cooling rate. The reference-cooling rate of each experiment is shown at the left-hand side of each curve

also the formation of mesophase is slowed down if the content on 1-butene is increased [40].

The evaluation of transition temperatures by visual inspection of the cooling curves relies on the recognition of the delay of the exponential decrease of the sample temperature versus time. This approach is disadvantageous since it is operator dependent and since weak transitions may even not be recognized. An advantageous approach for detection of the phase transition during cooling is the analysis of the temperature-dependence of cooling rate. Phase transitions which are connected with a release of latent heat are recognized by local minima which then can reliably be evaluated regarding their temperature. In Fig. 2a and b are shown the dependencies of the cooling rate on the sample temperature for selected data sets of Fig. 1a and b. The curves are arranged for optimum presentation of the decrease of the transition temperatures with increasing cooling rate, with the reference-cooling rate indicated at the left-hand side of each curve. Though data are noisy due to the nature of the experiment, in particular in case of the copolymer iPP-But.6, two separate ordering processes are unambiguously identified. As pointed out earlier in initial discussion of the cooling curves, and as will be evidenced below by X-ray analysis, the high- and low-temperature processes are crystallization and mesophase formation, respectively.

Wide-angle X-ray scattering

Figure 3 shows a series of WAXS curves obtained during cooling of iPP-But.6 at reference-cooling rates of 7 K s^{-1} (a) and 67 K s^{-1} (b). The corresponding cooling curves and dependencies of the cooling rate versus sample temperature in Figs. 1a and 2a, respectively, are marked with an asterisk for easy assignment of data sets.

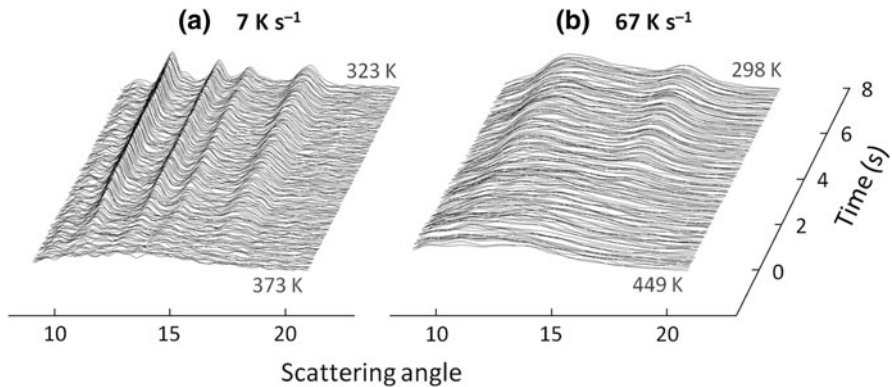


Fig. 3 WAXS curves of iPP-But.6 measured between 373 and 323 K, during cooling at a reference-cooling rate of 7 K s^{-1} (a) and measured between 449 and 298 K, during cooling at a rate of 67 K s^{-1} (b). The stacking of curves is linear versus time with an increment of 50 ms, covering a period of 8 s. The corresponding cooling curves in Fig. 1a and dependencies of the cooling rate versus temperature in Fig. 2a are marked with an *asterisk*

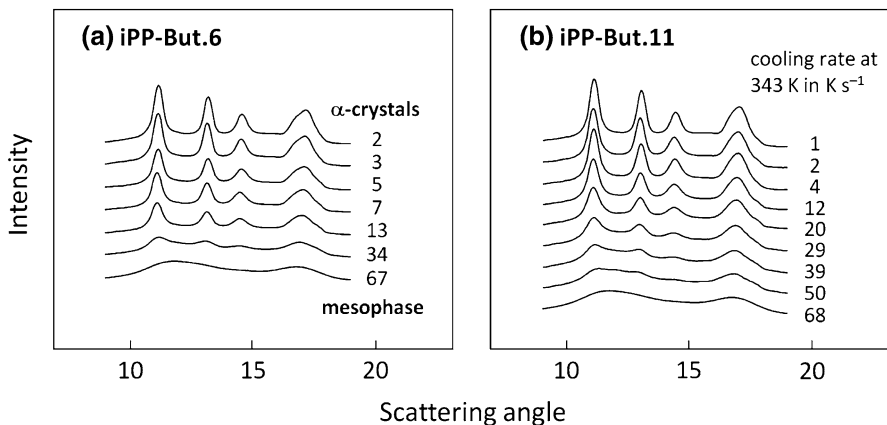


Fig. 4 WAXS patterns of iPP-But.6 (a) and iPP-But.11 (b) obtained at ambient temperature after cooling at different rate, as indicated at the right-hand side of each curve

It is emphasized again at this occasion that the cooling curves in Fig. 1a and the WAXS data of Fig. 3 were measured simultaneously, ultimately providing valuable information about the structure which forms at a particular transition temperature and cooling rate. Actually, in Fig. 3a and b are shown selection of WAXS patterns only, collected during a period of 8 s, covering the temperature range of the phase transformation. The time-increment between two consecutive curves is 50 ms, that is, a total of 160 curves have been plotted. In the experiment of Fig. 3a, the sample is in the molten state at 373 K, and at 342 K the characteristic peaks of the monoclinic α -structure appear. Obviously, as has initially been speculated on

discussion of the data of Figs. 1 and 2, cooling at 7 K s^{-1} still allows crystallization and is too slow to permit mesophase formation. In contrast, the experiment of Fig. 3b proves that on cooling at 67 K s^{-1} , crystallization is completely suppressed. Instead, mesophase forms at lower temperature of about 310 K. In fact, temperature-resolved WAXS data have been collected during all cooling experiments shown in Fig. 1 and were analyzed regarding the onset temperature of the ordering process, and the specific polymorph formed.

An overview about the effect of the cooling rate on the X-ray structure of the two iPP copolymers containing 6 and 11 mol.% 1-butene is provided with Fig. 4a and b, respectively. It shows WAXS patterns, intensity as a function of the scattering angle, measured at ambient temperature immediately after completion of the cooling segment, with the exposure time increased from 50 ms to 15 s in order to reduce the noise of the data. The curves show that in both cases, iPP-But.6 and iPP-But.11, the increase of the cooling rate results in replacement of crystals by mesophase. The transition from formation of a semicrystalline structure to a semimesomorphic structure, apparently, is completed at a cooling rate of about 50 K s^{-1} . Cooling of iPP-But.6 and iPP-But.11 at 67 or 68 K s^{-1} , respectively, did not permit formation of crystals, as can unambiguously be deduced from the corresponding X-ray scans shown in Fig. 4.

Effect of cooling rate on transition temperatures and polymorphism

Figure 5a and b shows the temperature of ordering of iPP-But.6 and iPP-But.11, respectively, as a function of the rate of cooling, summarizing the information discussed with Figs. 1, 2, 3, and 4. Importantly, Fig. 5 contains additional information about the polymorph formed, detected for the first time in situ, during cooling of the sample. Formerly, the analysis of the cooling-rate dependence of

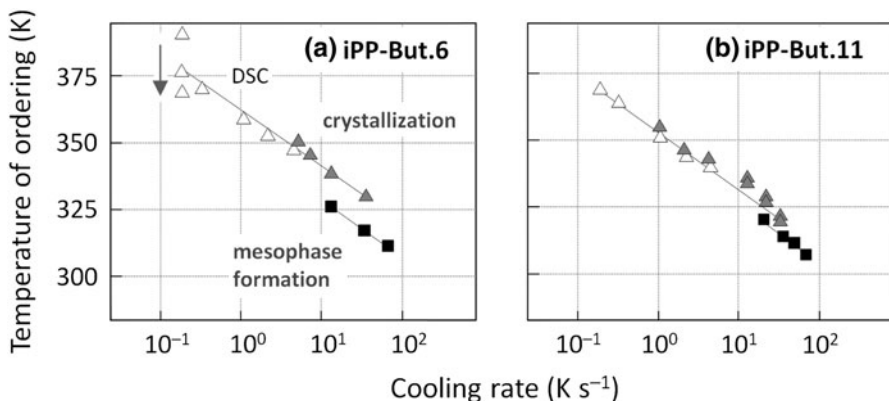


Fig. 5 Temperature of ordering of iPP-But.6 (a) and iPP-But.11 (b) as a function of cooling rate, with the triangles and squares indicating crystallization and mesophase formation, respectively. The white triangles represent data obtained by differential scanning calorimetry in separate studies [31, 33]. The gray-filled triangles and black squares represent data measured in this work by analysis of both cooling curves and temperature-resolved X-ray experiments

transition temperatures was performed by FSC which did not yield information about the X-ray structure [33], even after completion of the experiment. The former approach of non-isothermal solidification of films and subsequent analysis of the structure, without the ability to detect transition temperatures during the preparation [31, 32], was similarly incomplete.

In Fig. 5, the triangles denote formation of crystals, while mesophase formation is indicated by the squares. The white triangles represent data measured by differential scanning calorimetry (DSC) in a separate study [33], while the gray triangles and black squares represent data observed in this work. It can be seen that the crystallization temperatures obtained during linear cooling in a DSC and by non-linear cooling in the experiments of the present work fit a single curve and even overlap each other. Crystallization is only observed on cooling slower than about $30\text{--}50\text{ K s}^{-1}$. Cooling at 67 or 68 K s^{-1} , that is, at the highest, in this work achieved cooling rates, only resulted in mesophase formation (see Fig. 4). In case of the iPP homopolymer, in contrast, crystallization was only inhibited on cooling faster than 150 K s^{-1} [5].

Furthermore, the data of Fig. 5 provide the information that in the random propylene-1-butene copolymers of this study mesophase starts to form on cooling faster than about $20\text{--}30\text{ K s}^{-1}$ (see black squares). Apparently, also the lower cooling-rate limit to obtain mesophase is decreased if compared to results obtained on the iPP homopolymer. In case of the homopolymer, mesophase formation was detected only on cooling faster than 90 K s^{-1} [5]. Analysis of the upper cooling-rate limit to suppress even mesophase formation was not possible in the present work since the temperature of the air used for cooling was higher than the glass transition temperature. As a consequence, mesophase is formed even on fastest cooling due to annealing at ambient temperature. Notwithstanding, critical cooling rates to suppress both crystallization and mesophase formation in the copolymers of this work have been evaluated by FSC, which allowed fast cooling to temperatures below the glass transition. It has been found that in random copolymers of propylene and 1-butene lower cooling rates are needed to obtain fully amorphous samples than in case of the homopolymer. This observation was then confirmed by a quantitative analysis of the kinetics of isothermal mesophase formation at 300 K , which showed that presence of 1-butene in the iPP chain slows down this process [40].

Summarizing the observation of critical cooling rates from the data of Fig. 5, Table 1 shows the minimum cooling rate required to obtain mesophase and the maximum cooling rate to permit crystallization.

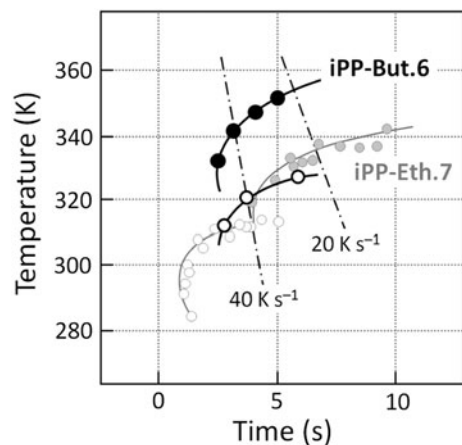
Table 1 Minimum cooling rate required for mesophase formation ($CR_{\min,\text{mesophase}}$) and maximum cooling rate to permit crystallization ($CR_{\max,\text{crystallization}}$) as a function of concentration of 1-butene

| Content 1-butene (mol.%) | $CR_{\min,\text{mesophase}}$ (K s^{-1}) | $CR_{\max,\text{crystallization}}$ (K s^{-1}) |
|--------------------------|----------------------------------------------------|----------------------------------------------------------|
| 0 | 90 [5] | 150 [5] |
| 6 | 20–30 | 30–50 |
| 11 | 20–30 | 30–50 |

The data of Fig. 5 suggest furthermore that insertion of 1-butene co-units into the iPP chain has a greater effect on the kinetics of crystallization than on the kinetics of mesophase formation. At a given cooling rate, the decrease of the temperature of crystallization with increasing concentration of co-units is more pronounced than the decrease of the temperature of mesophase formation. In Fig. 5a, a decrease of the crystallization temperature of iPP on addition of 11 mol.% 1-butene by about 25 K on cooling at 0.17 K s^{-1} is indicated with the vertical, downward directed arrow. In contrast, the temperature of mesophase formation of iPP on cooling at about 90 K s^{-1} decreases by less than 10 K on addition of 11 mol.% 1-butene. As a consequence, the temperature gap between the crystallization temperature and temperature of mesophase formation decreases with increasing concentration on 1-butene. The data of Fig. 5b show that crystallization and mesophase formation in iPP-But.11 almost occur at identical temperature on cooling at rates between 20 and 50 K s^{-1} . In case of the homopolymer, a gap of 30–40 K between the temperatures of crystallization and mesophase has been measured (see Fig. 6 in ref. [5]).

Finally, the data of the present study about structure formation of random copolymers of propylene and 1-butene on cooling at different rate are compared with data obtained on a random copolymer of propylene with 7 mol.% ethylene [35]. Though the mechanisms of structure formation in these copolymers qualitatively are identical, there are observed quantitative differences regarding transition temperatures and critical cooling rates to obtain crystals or mesophase. For discussion of the effect of the type of co-units, transition temperatures were replotted in a continuous cooling transformation (CCT) diagram. From this diagram, information can be gained about the temperature and time of the approximate onset of the phase transition at a specific cooling history. The gray circles represent data obtained on a random copolymer of propylene with 7 mol.% ethylene (iPP-Eth.7) in a former study [35], while the open and filled black circles represent data measured on iPP-But.6 in this work. In order to make the data sets comparable, results obtained in the present study were shifted by 0.5 s to longer time since the cooling experiments started at an about 15–20 K lower temperature than in the experiments reported in the literature [35].

Fig. 6 Continuous cooling transformation (CCT) diagram for random copolymers of propylene and 7 mol.% ethylene (iPP-Eth.7) [35] or propylene and 6 mol.% 1-butene (iPP-But.6). Crystallization and mesophase formation are indicated by the *filled* and *white* circles, respectively. The *dot-dashed* lines indicate linear cooling at 20 K s^{-1} and 40 K s^{-1} , starting at a temperature of 468 K



The comparison of the various data sets in Fig. 6 reveals that addition of approximately equivalent amount of ethylene or 1-butene co-units—7 mol.% ethylene versus 6 mol.% 1-butene—leads to significantly different transition temperatures and times. Copolymers which contain ethylene co-units crystallize at distinctly lower temperature and later than copolymers which contain 1-butene co-units of almost identical content. For example, cooling a quiescent melt from 468 K at a rate of 20 K s^{-1} leads to crystallization at about 353 K in case of the copolymer iPP-But.6 and only at almost 20 K lower temperature of about 336 K in case of iPP-Eth.7. Furthermore, as can directly be read from the virtual cooling experiment using a rate of 40 K s^{-1} , the minimum cooling rate to avoid crystallization is lower for the copolymer containing ethylene co-units. Cooling at 40 K s^{-1} leads to formation of crystals and mesophase at about 340 and 320 K, respectively, in the random copolymer containing 6 mol.% 1-butene while there is only formation of mesophase in case of the random copolymer containing 7 mol.% ethylene, occurring at about 310–315 K. Regarding the comparison of the crystallization behavior of random copolymers of propylene with ethylene or 1-butene, we are aware about possible influence—besides the chemical composition—of molecule parameters like molar mass, polydispersity, or stereo-regularity. The two copolymers compared in Fig. 6 exhibit almost identical molar mass of 225 (iPP-But) and 310 kDa (iPP-Eth) and almost identical polydispersity of 3.1 (iPP-But) and 3.4 (iPP-Eth). Information about the stereo- and regio-regularity were not yet available to us, and require therefore further work in order to quantify an effect of these parameters on structure formation at rapid cooling.

Summary

In the present study, the formation of crystals or mesophase in random copolymers of propylene with 1-butene during continuous cooling has been monitored for the first time by simultaneous recording of cooling curves and temperature-resolved X-ray scattering data. Besides the goal of gaining information about details of the dynamics of solidification and the polymorphism of propylene-based random copolymers, the performed experiments also served for demonstration of recent advances of X-ray instrumentation and polymer characterization techniques. The use of intense and brilliant X-ray radiation, as is available at synchrotrons, in combination with new detectors, permitted recording of two-dimensional X-ray images at a time-resolution of the order of magnitude of milliseconds, which, for example, opens new opportunities for the analysis of phase transitions. In our particular case, structure formation in propylene-1-butene copolymers was followed on relatively fast cooling at rates between about 10^0 and 10^2 K s^{-1} , which ultimately allowed detection of a critical cooling rate at which crystallization is replaced by mesophase formation. For the two copolymers of this work, containing 6 and 11 mol.% 1-butene, mesophase forms on cooling at rates as low as 20 K s^{-1} while crystallization is completely suppressed if the cooling rate exceeds about 50 K s^{-1} . As such, the critical cooling rate for replacement of crystals by mesophase is lower than in case of the homopolymer which has been attributed to

faster crystallization of the latter. Furthermore, it has been concluded by transfer of transition temperatures and times into a continuous cooling transformation (CCT) diagram that crystallization of random copolymers containing ethylene of roughly identical molar concentration, on cooling at identical rate, occurs at distinctly lower temperature than in case of the presence of random copolymers containing 1-butene co-units. This observation is in agreement with observation of an even lower critical cooling rate for complete suppression of crystallization in case of random copolymers containing ethylene.

Acknowledgments Financial support by the Deutsche Forschungsgemeinschaft (DFG) for two of the authors (DM, RA) and by ESRF is gratefully acknowledged. Furthermore, we thank the team of the beamline BM26B/Dubbe at ESRF for their assistance in temperature-resolved X-ray measurements.

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