

# Effect of co-unit type in random propylene copolymers on the kinetics of mesophase formation and crystallization

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**Abstract** Fast scanning chip calorimetry has been employed to study the effect of the type and concentration of co-units on the rate of mesophase formation and crystallization in random isotactic copolymers of propylene and 1-alkenes, including ethylene, 1-butene, 1-hexene, and 1-octene. The dependence of the rate of ordering on temperature of the propylene homopolymer shows two distinct maxima around 300 and 340–350 K which are related to mesophase formation and crystallization, respectively. Addition of 1-alkene co-units leads to a decrease of the maximum rate of both crystallization and mesophase formation. At comparable temperature and molar percentage of co-units in the propylene chain, ethylene, and 1-butene co-units cause less reduction of the maximum rate of ordering than 1-hexene or 1-octene co-units. The experimental observations are discussed in the context of possible incorporation of these chain defects into the ordered structures.

**Keywords** Polypropylene · Random copolymers · Fast scanning chip calorimetry · Crystallization

## Introduction

Since its first synthesis, more than 50 years ago, isotactic polypropylene (iPP) continues to attract both scientific and industrial attention [1–3]. A unique opportunity to control final material properties is possible through variation of the fraction, structure, morphology, and higher-order arrangement of crystals. Isotactic polypropylene can form different crystal

structures [4, 5], among which the monoclinic  $\alpha$ -form and mesophase structure are of primary interest in the present work. The structure of these polymorphs at the nanometer scale has been described in detail elsewhere [6–9] and the formation can effectively be controlled by the rate of solidification and/or supercooling of the isotropic melt before ordering. The cooling conditions to generate  $\alpha$ -crystals or mesophase were quantified either by analysis of the X-ray structure of samples cooled at different rate [10–12], or by analysis of the temperature of the phase transformation as a function of the rate of cooling using a fast scanning chip calorimeter [13, 14]. Fully amorphous and glassy iPP was obtained by cooling the relaxed melt below the glass transition temperature of 260–270 K at rates higher than about  $10^3 \text{ K s}^{-1}$ ; cooling at rates lower than about  $10^2 \text{ K s}^{-1}$  resulted in formation of monoclinic  $\alpha$ -crystals of lamellar morphology at relatively high temperatures/low supercooling, organized within a spherulitic superstructure [15, 16]. Solidification of the quiescent melt of iPP at rates between  $10^2$  and  $10^3 \text{ K s}^{-1}$ , ultimately, led to suppression of crystallization at low supercooling and formation of mesophase domains at high supercooling. The mesophase is of nonlamellar shape and does not exhibit a higher-order superstructure [10, 17, 18]. The recent introduction of fast scanning chip calorimetry (FSC) permitted precise evaluation of the temperature dependence of the kinetics of crystallization and mesophase formation in iPP. While crystallization is fastest around 340 K with a half time of the melt–crystal phase transition of about 0.5 s, mesophase formation occurs only between the glass transition temperature and about 330 K. The formation of the mesophase is faster than the crystallization process, with the maximum rate observed at around 300 K [19, 20].

Recently it has been shown that the morphology and higher-order organization of  $\alpha$ -crystals of iPP formed either directly from the melt at rather low supercooling or via

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annealing of the mesophase, initially formed at high supercooling, are distinctly different [21], affecting ultimate properties [22, 23]. This notwithstanding, it has also been demonstrated for the specific case of iPP that structure and properties can effectively be tailored by variation of the chemical microstructure including the incorporation of constitutional defects like ethylene, 1-butene, 1-hexene, or 1-octene into the iPP chain [24]. There exist numerous reports about the effect of 1-alkene constitutional defects on structure formation, however, with emphasis put on crystallization at low supercooling/cooling rate [25–33]. In contrast, only few investigations have been performed focusing on solidification of random copolymers of propylene and 1-alkenes at high supercooling, leading to formation of the mesophase [34–37]. It is a general observation, that addition of 1-alkenes into the iPP chain causes a decrease of the crystallization rate and crystallinity. However, due to different degree of inclusion of co-units into crystals [38], the hindering of crystallization is larger in case of 1-hexene and 1-octene co-units compared to ethylene or 1-butene. For random copolymers containing ethylene and 1-butene, similar as in case of the iPP homopolymer, formation of mesophase at high supercooling has been confirmed. In addition, based on non-isothermal fast X-ray experiments and FSC, a decrease of the rate of mesophase formation due to presence of these co-units has been suggested [35, 36]. Regarding the effect of 1-hexene and 1-octene co-units on mesophase formation, as far as we are aware, there exist no reports. In this communication, we present therefore results of a comparative and quantitative study about the effect of the type and content of 1-alkene co-units in the iPP chain on the kinetics of isothermal mesophase formation and crystallization in a wide range of temperatures using FSC.

## Experimental

Table 1 contains data about the type and concentration of 1-alkene co-units of the samples analyzed in the present work. Additionally, information about the molar mass and the polydispersity are provided. Accordingly, we employed two isotactic homopolymers from Montell Polyolefins (iPP-M) and Borealis (iPP-B), in particular in order to qualitatively trace effects related to different synthesis routes/polydispersity of the molar mass distribution. The random copolymers containing ethylene, 1-hexene, and 1-octene were obtained by Borealis, and copolymers containing 1-butene were purchased from Sigma Aldrich.

For analysis of the temperature-dependence of the kinetics of isothermal mesophase formation and crystallization, we employed a power compensation differential fast scanning chip calorimeter Flash DSC 1 from Mettler Toledo in conjunction with a Huber intracooler TC45. Specimens with

a thickness of about 15  $\mu\text{m}$  and a mass of about 200 ng have been prepared from initially compression-molded films, with the scheme of estimation of the sample mass reported earlier [39, 40]. Before placing the sample onto the membrane of the sample calorimeter, a thin layer of silicon oil was spread on the sensor to improve the thermal contact to the sample. The furnace was purged with dry nitrogen at a flow rate of 30  $\text{mL min}^{-1}$ . Further details of the specific instrument used including calibration, accuracy, or sample preparation are reported elsewhere [40–43]. The specimens were heated to 473 K, kept at this temperature for a period of 0.1 s and subsequently cooled at  $10^3 \text{ K s}^{-1}$  to the temperature of analysis between 250 and 400 K.

## Results and discussion

Figure 1 is a plot of the temperature–time profile used for FSC analysis of the kinetics of isothermal crystallization and mesophase formation of the homo- and copolymers listed in Table 1. The specimens were cooled from 473 K at a rate of  $10^3 \text{ K s}^{-1}$  to the temperature of analysis, with the selected cooling rate ensuring absence of ordering before the isothermal segment has been reached. The exothermic heat flow caused by the isothermal liquid–mesophase or liquid–crystal phase transformation—depending on the pre-selected temperature—was then recorded as a function of time. In the upper part of Fig. 1 are exemplarily shown heat flow-rate data collected at 300 K on the iPP homopolymer (top curve) and random copolymers containing about 1 mol% 1-octene (iPP-Oct.1, center curve) and 3 mol% 1-octene (iPP-Oct.3, bottom curve).

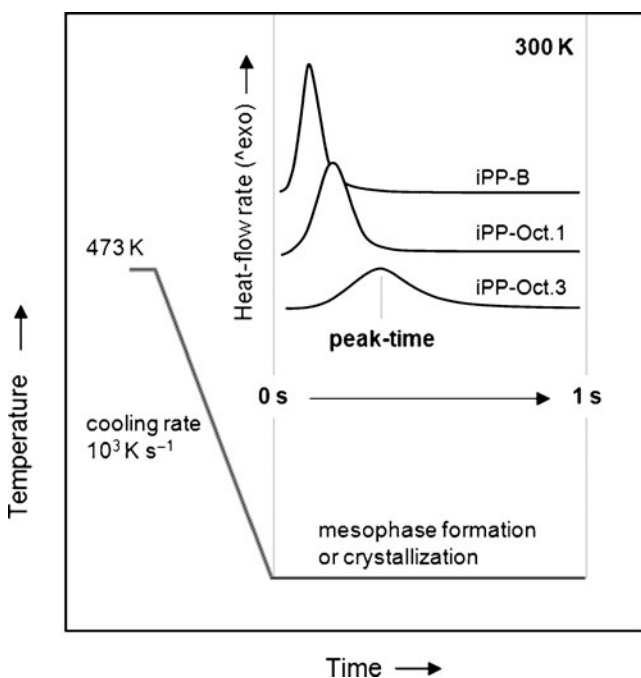
It can be seen that the phase transformation in all of these examples seems completed within 1 s, and that the transition is fastest in the homopolymer; addition of about 1 or 3 mol% 1-octene leads to a distinct delay of the formation of mesophase. For quantification of the kinetics of the phase transition, the peak time, as defined and illustrated in Fig. 1, has been determined and plotted as a function of the temperature of analysis and composition of the copolymers. For the curves shown in Fig. 1, the peak time is less than 0.10 s in case of the iPP homopolymer, and 0.20 and 0.35 s in case of iPP-Oct.1 and iPP-Oct.3, respectively. Similar experiments have been performed for all homo- and copolymers listed in Table 1, covering the temperature range from 250 to 400 K.

Figure 2a and b show the peak time of the phase transformation from the melt into mesophase or crystals as a function of the temperature of analysis. In Fig. 2a are plotted data observed on the homopolymer iPP-M and random copolymers of propylene with ethylene (left) or 1-butene (right), and in Fig. 2b, correspondingly, are plotted data observed on the homopolymer iPP-B and random copolymers of propylene with 1-hexene (left) or 1-octene (right). The calorimetrically measured peak time is indirectly proportional

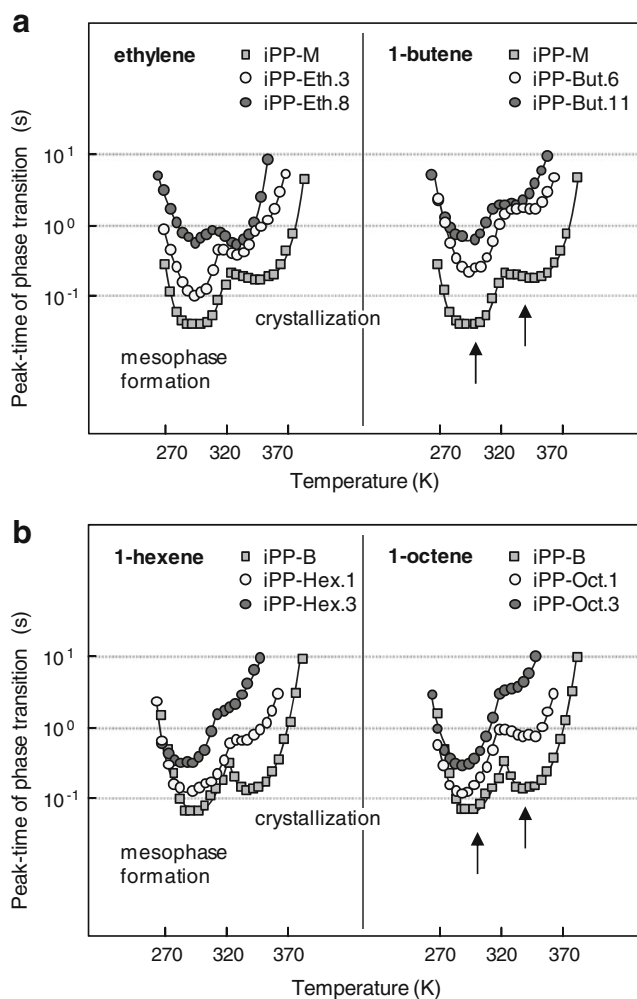
**Table 1** List of samples used in the present work, including information about the type of co-units, concentration of co-units, and approximates of the molar mass and polydispersity (Borealis 2010, personal communication; Basell 2001, personal communication)

Sample	Type of co-units	Content of co-units mol%	Molar mass $\text{kg mol}^{-1}$	Polydispersity
iPP-M	–	–	373	6.2
iPP-B	–	–	300	2.0
iPP-Eth.3	Ethylene	3.4	400	3.8
iPP-Eth.8	Ethylene	7.5	400	3.8
iPP-But.6	1-Butene	6.0	225	3.1
iPP-But.11	1-Butene	10.9	225	3.1
iPP-Hex.1	1-Hexene	0.9	230	2.0
iPP-Hex.3	1-Hexene	2.9	230	2.0
iPP-Oct.1	1-Octene	0.9	250	2.0
iPP-Oct.3	1-Octene	2.4	250	2.0

to the crystallization rate which, regarding its temperature dependence, has frequently been modeled using the Turnbull–Fisher equation, taking into account the thermodynamic driving force for the phase transition and the mobility of chain segments [44, 45]. Accordingly, it is expected that the crystallization rate and peak time pass a maximum or minimum, respectively, when plotted as a function of temperature. The dependence of the peak time of ordering versus temperature has been evaluated and discussed in earlier reports for iPP [9, 19, 20]; two minima were observed which are related to heterogeneous nucleation and crystallization at high



**Fig. 1** Schematic of the temperature–time profile of FSC analysis of the kinetics of isothermal mesophase formation or crystallization, and heat flow rate as a function of time collected isothermally at an analysis temperature of 300 K on the iPP homopolymer and random copolymers of propylene and 1-octene. The heat flow rate data serve as an example only and were recorded on all samples listed in Table 1 at temperatures between 250 and 400 K



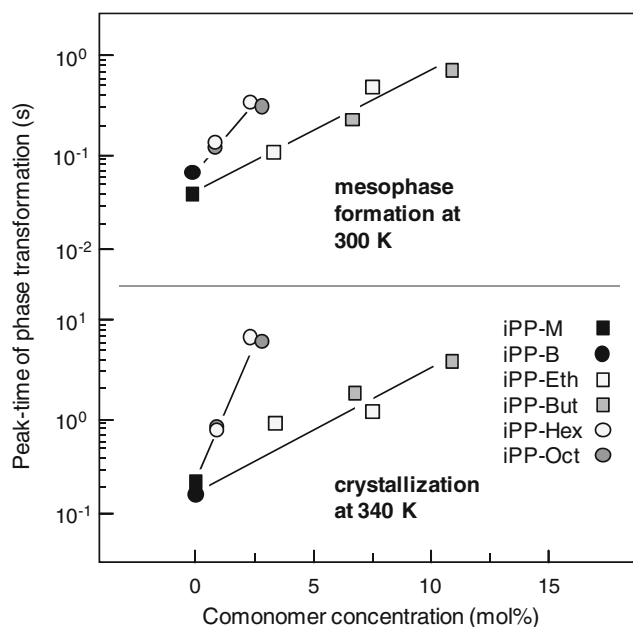
**Fig. 2** **a** Peak time of the phase transition from the melt into mesophase or into crystals as a function of temperature for the iPP-M homopolymer and random copolymers of propylene with ethylene (*left*) and 1-butene (*right*). **b** Peak time of the phase transition from the melt into mesophase or into crystals as a function of temperature for the iPP-B homopolymer and random copolymers of propylene with 1-hexene (*left*) and 1-octene (*right*)

temperature, and homogeneous nucleation and mesophase formation at low temperature. According to the data shown in Fig. 2a and b, mesophase formation for the iPP homopolymers of the present work is fastest around 300 K while crystallization is fastest around 340–350 K. This observation is almost independent on the exact source and therefore molecular characteristics of the iPP homopolymers. Note that the homopolymer iPP-B is a metallocene-catalyzed grade with distinctly lower polydispersity than the homopolymer iPP-M. However, the different polydispersity has only negligible effect on the ordering kinetics. As reference for discussion of the effect of copolymerization on the ordering kinetics we plotted in Fig. 2a data of the iPP-M homopolymer and in Fig. 2b data of the iPP-B homopolymer. The reason behind this choice is that the iPP-Hex and iPP-Oct copolymers shown in Fig. 2b are of identical source as iPP-B and therefore of similar molecular characteristics.

The data of Fig. 2a and b demonstrate that incorporation of 1-alkene co-units into the iPP chain does not change the bimodal nature of the relationship between the rate of ordering and temperature. As such, it is concluded that structure formation of the iPP-based random copolymers investigated in this work qualitatively obeys similar rules as in the iPP homopolymer. At low supercooling, the melt transforms via heterogeneous nucleation to crystals and at high supercooling mesophase forms in conjunction with homogeneous nucleation. For iPP-Eth and iPP-But copolymers, detailed structural analyses were performed in the past [34–36], supporting the above interpretation. Though the transition from the melt into ordered phase in case of the copolymers qualitatively seems to resemble that of the iPP homopolymer, quantitative differences regarding the rate of phase transformation can be identified. The experimental results prove that both crystallization and mesophase formation are slower in the copolymers, with the rate of the phase transition decreasing with increasing content on co-units; the data sets related to the copolymers in Fig. 2a and b are shifted vertically to longer peak times, compared to that of the homopolymers. Furthermore, it seems that incorporation of co-units has a larger effect on the kinetics of crystallization than on the kinetics of mesophase formation, at least in case of copolymers containing 1-hexene and 1-octene co-units. Most striking, however, is the observation of a distinct influence of the type of co-units on the reduction of the rate of both crystallization and mesophase formation. For example, in order to increase the peak time of crystallization at around 340–350 K from 0.1 to 10 s, it is required to add, roughly, either 10–15 mol% ethylene or 1-butene but only about 3 mol% 1-hexene or 1-octene; similar tendency is observed regarding the liquid–mesophase transition. Note that the experimental observation of a lowering of the rate of ordering/crystallization at a given temperature cannot be related to a change of the segmental mobility since addition

of 1-alkene co-units is connected with a decrease of the glass transition temperature. From this point of view, an increase of the ordering/crystallization rate would be expected which is not the case.

For further illustration of the effect of the type of co-units on the rate of crystallization and mesophase formation selected peak time data of Fig. 2a and b are replotted in Fig. 3 as a function of the molar percentage of co-units. In the upper part of Fig. 3 is shown the increase of the peak time of mesophase formation at 300 K due to incorporation of 1-alkene chain defects while in the lower part is shown the increase of the peak time of crystallization at 340 K. The selection of the temperatures of 300 and 340 K for the comparison of peak times in Fig. 3 is based on the observation that at these temperatures the rates of the liquid–mesophase and liquid–crystal phase transition, respectively, are fastest in the iPP homopolymer, as indicated in Fig. 2a and b by the vertical arrows. The specific graphical representation of peak time data in Fig. 3 suggests qualitatively different influence of ethylene and 1-butene co-units on the one hand (squares), and 1-hexene and 1-octene co-units on the other hand (circles), on the kinetics of solidification of the melt; the classification of the type of co-units has been emphasized with the lines in Fig. 3, included for easy recognition of the different effect of the various co-units on the kinetics of phase transitions. The data demonstrate quantitatively that addition of 1-hexene or 1-octene co-units into the iPP chain affects much stronger the kinetics of both crystallization and mesophase formation than the addition of ethylene or 1-butene co-units.



**Fig. 3** Peak time of the phase transformation from the melt into mesophase at 300 K (*top*) or into crystals at 340 K (*bottom*) as a function of the comonomer concentration

It is generally expected that ordering processes in random copolymers are slower than in the respective homopolymer [45–47]. We assume that the observation of different degree of hindering of molecular ordering in the various copolymers studied is related to different amount of incorporation of co-units into crystals or mesophase. Though unequivocal knowledge about incorporation of 1-alkene comonomers into the crystalline phase of iPP is not available, there seems agreement that among the various 1-alkene comonomers investigated 1-butene co-units are most favorable inserted into the ordered phase [29, 38]. Regarding ethylene co-units, it is also repeatedly reported that these co-units participate on crystallization despite there may be partial segregation at the crystal growth front. Conformational energy calculations revealed a higher increase of the potential energy of helical chains in presence of ethylene co-units compared to 1-butene co-units [27]. Most controversial seems the behavior of copolymers containing 1-hexene and 1-octene co-units; there are few reports which suggest partial inclusion into the crystal phase [26, 38], however, most studies favor complete segregation and exclusion from ordering [32, 33, 48–50]. The data of Fig. 3 provide experimental evidence that insertion of ethylene and 1-butene co-units into the iPP chain leads to less reduction of the rate of both crystallization and mesophase formation than insertion of 1-hexene or 1-octene co-units which is in qualitative agreement with the generally accepted sequence of tendency for incorporation of co-units into ordered structure.

Though a comparison of the effect of the type co-units on the isothermal crystallization kinetics is available in the literature [29], the novelty of the present work is the inclusion of the temperature ranges of maximum crystallization rate and maximum mesophase-formation rate in the present analysis; in prior work, these temperature ranges were omitted, likely due to instrumental reasons. The data of Fig. 3 prove that the kinetics of mesophase formation in random copolymers is similarly affected by the co-unit type as the crystallization process. However, qualitative inspection of the data observed on iPP-Hex and iPP-Oct copolymers in Figs. 2b and 3 suggests less hindrance in case of mesophase formation since the increase of the minimum peak time of mesophase formation on addition of 1-hexene or 1-octene is less pronounced than in case of the minimum peak time of crystallization. It may be speculated that this observation is caused by partial though not necessarily complete incorporation of these co-units into the mesophase, which, in turn, is expected to cause less delay of the ordering process. In case of ethylene and 1-butene co-units, the slowing down of crystallization and mesophase formation seems similar, providing no indication about different tendency of inclusion of these co-units into crystals and mesophase. Anyway, it is straightforward to assume incorporation of ethylene and 1-butene co-units during fast mesophase formation in the shed

of light that even during slower crystallization there is no exclusion of these co-units from the ordering process.

## Summary

In the present study, the kinetics of isothermal crystallization and mesophase formation in random copolymers of propylene with ethylene, 1-butene, 1-hexene, or 1-octene has been analyzed as a function of temperature. The use of the new technique of fast scanning chip calorimetry permitted analysis of the kinetics of the liquid–crystal and liquid–mesophase transitions in a wide range of temperatures including the temperature ranges of maximum rate of crystallization and mesophase formation. The rate of ordering shows a bimodal distribution versus temperature which in the past for the specific case of the iPP homopolymer has been explained with a change from heterogeneous nucleation and crystallization at low supercooling to homogeneous nucleation and mesophase formation at high supercooling. The data of the present work show that in random copolymers of propylene with 1-alkenes the general nature of structure formation is preserved, that is, for all copolymers similar bimodality of the rate of ordering has been confirmed. Quantitative inspection of the rate of ordering proves that both crystallization and mesophase formation are distinctly slower in the studied random copolymers compared to the iPP homopolymer. Moreover, it has been found that presence of ethylene or 1-butene co-units in the iPP chain affects the rate of ordering to a lesser degree than the presence of identical amount of 1-hexene or 1-octene co-units. Based on the knowledge available in the literature, we interpret the different influence of the various types of co-units on the ordering kinetics by their tendency of being incorporated into the crystal phase and the mesophase. As such, we consider the data of the present work of being in qualitative agreement with the notion that ethylene and 1-butene co-units participate easier on the ordering process than 1-hexene and 1-octene co-units. Finally, it has been observed that in case of random copolymers containing 1-hexene or 1-octene the reduction of the rate of mesophase formation is less pronounced than the reduction of the crystallization rate; it is suggested that these co-units, at least partially, are entrapped into the mesophase on its fast formation.

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